Studies on New Covalently and Non-covalently Linked Functional Hybrids of Porphyrins and Carbon Nanomaterials

Boyang Mao

A thesis submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at University of Bath
June, 2015

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Signed on behalf of the Faculty of Science of………………………….
List of publications resulting from this PhD


List of poster presented during this PhD


2. Boyang Mao, Benjamin J. Hodges, Rory L. Arrowsmith, José Alberto Ribeiro Martins, Paul R. Raithby and Sofia I. Pascu, Supramolecular Complexes of Zn(II)-porphyrin and CarbonNanomaterials, RSC Macrocyclic and Supramolecular Chemistry Meeting, MASC 2013, 16th – 17th December 2013, University of Glasgow, Glasgow, UK.

Abstract

This thesis focuses on the design and delivery of new carbon-based nanohybrid dyes of relevance to the search for affordable solar energy harvesting solutions. New hybrid nanomaterials incorporating covalently and non-covalently linked porphyrins grafterd onto carbon nanomaterials such as single-walled carbon nanotubes (SWNTs), graphene oxide (GO) and thermally reduced graphene oxide (TRGO) were synthesised and characterised using a range of spectroscopy methods and microscopies. The synthesis of aryl-substituted porphyrins, achieved on a laboratory scale suitable for further modification with carbon nanomaterials and functional materials development is also discussed.

Chapter one is a literature review, which constitutes the thesis introduction and background to this research, with a view towards highlighting the potential of porphyrins and related nanomaterials in the quest for sustainable chemistry applications and solar cells technologies.

Chapter two reports on the synthesis of the carbon nanomaterials used hereby and includes discussions on the modified protocols for graphene oxide synthesis and advanced purification of single-walled carbon nanotubes as well as the surface modification of single-walled carbon nanotubes. In chapter two, the strategy applied here for the reduction of graphene oxide is discussed and the achievement of the desired material demonstrated on the basis of the spectroscopic measurements performed, i.e. the synthesised materials were characterised by TEM/HRTEM and SEM whereas Raman spectroscopy was applied to bulk materials aiming to study the inner structure and purity on the nanoscale.

Chapter three describes the lab scale synthesis and characterisation of a free base porphyrin and Zn(II)-porphyrin. These were specifically selected for this study to
have two aryl thioacetate-functionalised side groups at meso-position, which can be employed as reaction sites in further transformations aimed to covalently link this to nano-particulate supports. The porphyrins chosen also incorporate four hexyl chains at the β-position, which was found to be necessary in order to increase the solubility of these porphyrins in common solvents which in turns was found to facilitate their purification on a lab scale with respect to the starting materials. The design was chosen aiming to prevent self-aggregation, minimise self-stacking on a carbon support and facilitate their binding to other materials in a supramolecular fashion. Chemistry is discussed for both the free base porphyrin and after the converted to Zn(II) metalloporphyrin. Attempts to incorporate Ga(III)Cl and In(III)Cl at the core of the ligand are also discussed. The spectroscopic measurements of light absorption and emission properties of the porphyrins, carried out by UV-vis and fluorescence microscopy are discussed and DFT calculations (gas phase) were included to investigate the electronic structure and HOMO-LUMO energy levels of the Zn(II)-porphyrin.

Chapter four presents a new strategy for the supramolecular complex formation at the exposure of single-walled carbon nanotubes (purified as described in Chapter 2) to the Zn(II)-porphyrin discussed in Chapter 3 above. Furthermore, in this chapter, the formation of a non-covalently linked Zn(II)-porphyrin@SWNTs hybrid and that of a new covalently linked Zn(II)-porphyrin@SWNTs nanomaterial was analysed and discussed. The surface morphology information of those complexes compared and contrasted using information obtained on the nanoscale by TEM and AFM techniques. Raman spectroscopy was carried out to study the inner structure of the complex materials. Upon its attachment onto the SWNTs surface, Zn(II)-porphyrin showed efficient fluorescence quenching and a strong red-shift of the Soret bands. Lifetime measurements using single-photon laser confocal fluorescence measurements on these materials deposited onto a thin film support were carried out to explore their potential application in photovoltaic devices.
**Chapter five** described the formation of a new nano-dimensional hybrid material, denoted Zn(II)-porphyrin@GO, formed at the non-covalent binding of Zn(II) porphyrins onto graphene oxides. This section describes the novel synthetic approach to a three dimensionally structured material, denoted porphyrin@TRGO (where thermally reduced graphene oxides were used to form the new supramolecular complex). This chapter aims to describe the steps taken towards the modification (or ‘decoration’) of graphene oxide surface with the Zn(II)-porphyrin through π-π stacking. A three-dimensional scaffold material based on RGO was achieved by a one-step hydrothermal reaction. Imaging using TEM, SEM and AFM techniques were applied to analyse the surface morphology modifications in the presence and absence of porphyrin layers.

**Chapter six** describes conclusions and proposes future works.

**Chapter seven** contains full experimental details for the work described in this thesis.

**The Appendix** contains some alternative microscopy images and data used in supporting the discussions and proposals for future work.
Acknowledgements

First, my many thanks to Dr. Sofia I. Pascu. Her supervision throughout my time here in University of Bath as both my PhD supervisor and as my older friend, has been the most reassuring, inspiring and enthusiastic that I could have hoped for.

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I very much appreciate the help and guidance of Prof Jonathan R Dilworth, University of Oxford, with the porphyrin synthesis and their complexation with carbon nanomaterials, and the best wishes for his health. I would like to thank Prof Stan Stanley W. Botchway and Dr. Pierre Burgos for their assistance in single photon confocal microscopy and Raman spectroscopy measurements at the Rutherford Appleton Laboratory. I thank Prof José Alberto Ribeiro Martins, University of Minho, for the guidance with porphyrin synthesis and Dr. Robert M. J. Jacobs, University of Oxford, for the help with AFM characterisation. I thank Prof Lin Hong, Tsinghua University, and her students for the training in Dye-sensitised solar cells device build up.

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Last, but certainly not least, I would like to thank my mother and wife, who have been greatest and nicest persons to support my PhD studies. I can’t finish this PhD without their help. I will do everything I can do to make them happy in the rest of my life.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>1D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>A</td>
<td>absorbance</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>Ar</td>
<td>aromatic</td>
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<tr>
<td>B3LYP</td>
<td>Hybrid-DFT exchange-correlation functions by Becke, and Lee-Yang-Parr</td>
</tr>
<tr>
<td>BHJs</td>
<td>bulk-heterojunctions solar cells</td>
</tr>
<tr>
<td>cm</td>
<td>centimetre</td>
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<tr>
<td>C₆₀</td>
<td>fullerene</td>
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<tr>
<td>COSY</td>
<td>correlation spectroscopy</td>
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<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
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<tr>
<td>DBU</td>
<td>1,8-Diazabicycloundec-7-ene</td>
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<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DMF</td>
<td>N,N’-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<tr>
<td>DPP</td>
<td>diketopyrrolopyrrole</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitised solar cell</td>
</tr>
<tr>
<td>DWNTs</td>
<td>double walled carbon nanotube</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>eq</td>
<td>equivalents</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray ionization</td>
</tr>
<tr>
<td>ETA</td>
<td>extremely thin absorbers</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
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<tr>
<td>FLIM</td>
<td>Fluorescence-lifetime imaging microscopy</td>
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<tr>
<td>f-SWNTs</td>
<td>functionalised SWNTs</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GO</td>
<td>graphene oxide</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HMQC</td>
<td>Heteronuclear Multiple Quantum Coherence</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
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<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin / equilibrium constant</td>
</tr>
<tr>
<td>k</td>
<td>kilo</td>
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<tr>
<td>K_a</td>
<td>binding constant</td>
</tr>
<tr>
<td>L</td>
<td>litre</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>m</td>
<td>milli / meter</td>
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<tr>
<td>M</td>
<td>molar / mega</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to-charge ratio</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>MSSC</td>
<td><em>meso</em>-superstructured solar cell</td>
</tr>
<tr>
<td>MWNT</td>
<td>multi-walled carbon nanotube</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons</td>
</tr>
<tr>
<td>n</td>
<td>nano</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
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<tr>
<td>OT</td>
<td>oligothiophene</td>
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<tr>
<td>OSCs</td>
<td>organic solar cells</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
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<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>PV</td>
<td>photovoltaic</td>
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<tr>
<td>RBM</td>
<td>radial breathing mode</td>
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<tr>
<td>rGO</td>
<td>reduced graphene oxide</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>SEAD</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SWNTs</td>
<td>Single-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<td>TLC</td>
<td>Thin layer Chromatography</td>
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<td>TPA</td>
<td>triphenylamine</td>
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<tr>
<td>US</td>
<td>ultrasound</td>
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<tr>
<td>UV-Vis</td>
<td>Ultraviolet visible spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>δ</td>
<td>chemical shift</td>
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<tr>
<td>τ</td>
<td>fluorescence lifetime</td>
</tr>
<tr>
<td>τ₁</td>
<td>major component of fluorescence lifetime</td>
</tr>
<tr>
<td>τ₂</td>
<td>minor component of fluorescence lifetime</td>
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<tr>
<td>ε</td>
<td>molar absorption coefficient</td>
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<td>λ</td>
<td>wavelength</td>
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<td>Description</td>
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<tr>
<td>$\lambda_{ex}$</td>
<td>excitation wavelength</td>
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<tr>
<td>$\lambda_{max}$</td>
<td>maximum wavelength of</td>
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<tr>
<td>$\mu$</td>
<td>micro</td>
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List of Compounds

1

![Chemical structure 1]

Chemical Formula: C_{11}H_{20}O_{2}
Exact Mass: 184.15
Molecular Weight: 184.28
m/z: 184.15 (100.0%), 185.15 (11.9%)

2

![Chemical structure 2]

Chemical Formula: C_{11}H_{11}NO_{4}
Exact Mass: 221.07
Molecular Weight: 221.21
m/z: 221.07 (100.0%), 222.07 (11.9%)

3

![Chemical structure 3]

Chemical Formula: C_{20}H_{27}NO_{2}
Exact Mass: 313.20
Molecular Weight: 313.44
m/z: 313.20 (100.0%), 314.21 (21.6%), 315.21 (2.2%)
Chemical Formula: C_{22}H_{22}NO_{4}
Exact Mass: 371.21
Molecular Weight: 371.48
m/z: 371.21 (100.0%), 372.21 (23.8%), 373.22 (2.7%)
Chemical Formula: $\text{C}_{23}\text{H}_{38}\text{N}_2$

Exact Mass: 342.30

Molecular Weight: 342.57

m/z: 342.30 (100.0%), 343.31 (24.9%), 344.31 (2.7%)

---

Chemical Formula: $\text{C}_8\text{H}_7\text{BrO}$

Exact Mass: 197.97

Molecular Weight: 199.05

m/z: 197.97 (100.0%), 199.97 (97.3%), 198.97 (8.7%), 200.97 (8.4%)

---

Chemical Formula: $\text{C}_{10}\text{H}_{10}\text{O}_2\text{S}$

Exact Mass: 194.04

Molecular Weight: 194.25

m/z: 194.04 (100.0%), 195.04 (10.8%), 196.04 (4.5%)
Chemical Formula: C_{66}H_{84}N_{4}O_{2}S_{2}
Exact Mass: 1030.62
Molecular Weight: 1031.56

m/z: 1030.62 (100.0%), 1031.62 (71.4%), 1032.63 (25.1%), 1032.62 (9.0%), 1033.62 (6.5%), 1033.63 (5.0%), 1034.62 (2.3%), 1031.62 (1.6%), 1031.62 (1.5%), 1032.62 (1.1%), 1032.62 (1.1%)

Chemical Formula: C_{66}H_{84}N_{4}O_{2}S_{2}Zn
Exact Mass: 1092.53
Molecular Weight: 1094.92

m/z: 1092.53 (100.0%), 1093.54 (71.4%), 1094.53 (57.4%), 1095.53 (41.0%), 1096.53 (38.6%), 1097.53 (27.5%), 1094.54 (25.1%), 1096.54 (14.4%), 1098.54 (9.7%), 1094.53 (9.0%), 1095.53 (8.4%), 1095.53 (6.5%), 1096.53 (6.0%), 1096.53 (5.2%), 1095.54 (5.0%), 1097.53 (3.7%), 1098.52 (3.5%), 1097.54 (2.9%), 1099.53 (2.5%), 1096.54 (2.3%), 1097.54 (2.1%), 1099.54 (1.9%), 1093.53 (1.6%), 1093.53 (1.5%), 1098.53 (1.3%), 1098.53 (1.3%), 1094.54 (1.1%), 1094.53 (1.1%)
Chemical Formula: $\text{C}_{66}\text{H}_{54}\text{ClInN}_4\text{O}_2\text{S}_2$

Exact Mass: 1178.48

Molecular Weight: 1179.81

m/z: 1178.48 (100.0%), 1179.48 (71.4%), 1180.47 (32.0%), 1180.48 (25.1%), 1181.48 (22.8%), 1180.47 (9.0%), 1182.48 (8.0%), 1181.48 (6.5%), 1181.49 (5.0%), 1176.48 (4.5%), 1177.48 (3.2%), 1182.47 (2.9%), 1182.48 (2.3%), 1183.47 (2.1%), 1183.48 (1.9%), 1179.48 (1.6%), 1179.47 (1.5%), 1178.47 (1.4%), 1180.48 (1.1%), 1178.48 (1.1%), 1180.48 (1.1%), 1179.48 (1.0%)

Chemical Formula: $\text{C}_{66}\text{H}_{54}\text{ClGaN}_4\text{O}_2\text{S}_2$

Exact Mass: 1132.50

Molecular Weight: 1134.72

m/z: 1132.50 (100.0%), 1133.50 (71.4%), 1134.50 (66.4%), 1135.50 (47.4%), 1134.50 (32.0%), 1134.50 (25.1%), 1135.50 (22.8%), 1136.49 (21.2%), 1136.50 (16.7%), 1137.50 (15.1%), 1134.49 (9.0%), 1136.50 (8.0%), 1135.50 (6.5%), 1136.49 (6.0%), 1138.50 (5.3%), 1135.51 (5.0%), 1137.50 (4.3%), 1137.51 (3.8%), 1136.49 (2.9%), 1136.50 (2.3%), 1137.49 (2.1%), 1138.49 (1.9%), 1137.51 (1.9%), 1133.50 (1.6%), 1138.50 (1.5%), 1133.50 (1.5%), 1139.49 (1.4%), 1134.50 (1.1%), 1135.50 (1.1%), 1139.50 (1.1%)

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Chemical Formula: C₆₀H₇₇N₄S₂Zn
Exact Mass: 1008.51
Molecular Weight: 1010.85
m/z: 1008.51 (100.0%), 1009.51 (67.1%), 1010.51 (57.4%),
1012.51 (38.6%), 1011.51 (38.5%), 1013.51 (25.9%), 1010.52
(22.1%), 1012.52 (12.7%), 1010.51 (9.0%), 1014.51 (8.5%),
1011.51 (8.4%), 1011.51 (6.1%), 1012.51 (5.7%), 1012.50
(5.2%), 1011.52 (4.8%), 1014.50 (3.5%), 1013.51 (3.5%),
1015.51 (2.3%), 1013.52 (2.3%), 1012.51 (2.0%), 1013.52
(1.9%), 1009.51 (1.6%), 1015.52 (1.5%), 1009.51 (1.5%),
1014.51 (1.3%), 1014.51 (1.1%), 1010.51 (1.1%)

Chemical Formula: C₄₄H₅₀N₄
Exact Mass: 614.25
Molecular Weight: 614.75
m/z: 614.25 (100.0%), 615.25 (47.6%), 616.25 (11.1%), 617.26
(1.7%), 615.24 (1.5%)
Chemical Formula: $\text{C}_{44}\text{H}_{10}\text{F}_{20}\text{N}_{4}$
Exact Mass: 974.06
Molecular Weight: 974.56
m/z: 974.06 (100.0%), 975.06 (47.6%), 976.07 (11.1%), 975.06 (1.5%)
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1.1 Sustainable energy

1.1.1 Overview of sustainable energy

Production and consumption of energy is a basic element in human’s daily life, and crucial to societal development. The demand for energy is increased continuously with the evolution of civilizations. The increase of human population, urbanization, modernization and technology development all go along with the increased demand of energy supply. It is predicted that the growth in global energy demand will rise harshly over the coming year rendering the current reliance on fossil fuels, which is a bottleneck for continuous economic growth worldwide.

Currently, the world heavily relies on fossil fuels to meet the vast majority of its energy needs. Fossil fuels, for instance oil, gas and coal, which were generated by natural processes such as anaerobic decomposition of buried, dead, organisms over million years, are providing almost 80% of the global energy demands.\(^1\) The fact that humanity faces is that the significant amount of energy currently being consumed across the world has adverse implications on the environment of the Planet. The dominant supplier of energy, fossil fuels, is placing a serious of bad effects on the ecosystem. The significant consumption of fossil fuels leads to the dramatically emission of greenhouse gas (for example: \(\text{CO}_2\), \(\text{CH}_4\) etc.), which impact directly on the environment and contribute to the climate change. It has been reported that 160,000 people die each year due to the side-effects of climate change, which includes malnutrition, malaria, spread of epidemic diseases etc. that follow in the wake of floods, droughts and warmer earth temperatures, and the numbers of victims may double by the end of 2020, according to World Health Organization.\(^1\)
It has been well known that the amount of fossil fuel generated by the current sources decrease and, by facing the difficult climate challenging, the current energy system is unable to cope with future energy demands. The production and consumption of nuclear energy, which is mainly employed in developed counties, together with fossil fuels are strictly linked to increased threats to biological diversity, environmental degradation that affects human health and quality of life and affects ecological balance. Therefore, if the rapidly increasing global energy needs are to be met without irrevocable environmental damage, there should have to be a worldwide drive to create and exploit energy systems that are not detrimental to the life of current and future generations and do not exceed the current carrying capacity of ecosystems. This situation become even crucial in the last two years, the change of crude oil price, which dramatically decreased from around 110 USD/bbl to around 50 USD/bbl, the natural gas fracking considerations and economic crisis all effect people paid less attention in sustainable energy development.

Sustainable energy sources, which are naturally replenished, inexhaustible and widely available on a human timescale such as sunlight, wind, rain, tides and geothermal heat, have the potential to provide energy services with almost nil emissions of both air pollutants and greenhouse gases. Sustainable energy can replace fossil fuels in four distinct areas: electricity generation, hot water/space heating, motor fuels, and rural energy services. Currently, sustainable energy is only contributing 13.5%\(^1\) the total energy needs. Sustainable energy resources have the capacity to meet the current and future energy requirement of the world and minimise the reliance of fossil or nuclear fuels.

The development and use of sustainable energy sources has a lot of benefits which includes enhancing diversity in energy supply markets, help reduce local and global environmental impacts and provide commercially alternative options to meet specific energy service demands, contribute to securing long-term sustainable energy
supplies and also creating new employment opportunities practically in developing country and rural area. It is also noticed that the cost of energy generated from these renewable resources is significantly reduced with the developing of high technology.

Over the last two decades, solar and wind energy systems have experienced a rapid growth and dominated the sustainable energy market. This rapid growth was contributed by several reasons, like the decreasing capital cost and continued improvement in performance characterisation. Compared with wind energy, solar energy is still being investigated and has huge potential in technology revolution. The economic and policy mechanisms for developing solar energy are all support the widespread dissemination and rapidly evolving. Chemists, material scientists and other physical scientists have started the race for the high performance materials of relevance to sustainable energy applications. Thus, in this project, the application of materials chemistry towards solar energy applications was the central interest.

1.1.2 Introduction of solar cells

Solar cells are devices which can convert sun light to electricity. As we know today, the photovoltaic (PV) devices produce significant amounts of power, which contributed the 13.5% of the total energy needs. Solar energy as an alternative source of renewable energy is becoming more and more prevalent especially giving that the fossil fuel, like oil and gas, on this planet are likely to be depleted within decades. It was reported by Michael Grätzel that if the conversion ratio of solar energy arrived on the Earth’s surface up to 0.1% with solar cells which have 10 % working efficiency, it will satisfy all currently population’s energy needs.

Although the solar energy generation promises a number of advantages as discussed above, to develop the photovoltaic technology into a scalable commercial progress and fully cover the needs of human population’s activities though this source alone remains a very big challenge. One of the reasons for this high cost generation
capital is due to the high price of raw materials need to produced PVS on a large scale. High quality silicon wafers are needed in current technology but the resulted device has a relatively low light converting efficiency compared with the traditional fossil fuel materials. All the current researches in solar industry are aiming to solve these problems, which includes developing new materials to limit the raw material cost or a new cell structure to increase the converting efficiency. Figure 1.1 gives an overview of the PV cells available on the market, as provided by several established suppliers, as well as ne SMEs, and their related preference.

Figure 1.1: The efficiency of record best research performance solar cells in each of the primary technologies.\(^5\)

In 1839, Edmund Bequerel\(^6\) discovered the photovoltaic effect which describes the conversion of sun light into electricity. This discovers leads to the foundation stone of the development of solid state photovoltaic system. Willoughby Smith then later discovered the photovoltaic effect in selenium in 1873 and William G.
Adams, in 1876, investigate the illuminating effect given by a junction between selenium and platinum. These two discoveries lead to the first development of selenium solar cell in 1877. Until 1904, Albert Einstein theoretically explained the photovoltaic effect and was later awarded with Nobel Prize for his work in 1921. The largely development of solar cell did not occurs until after further research work, like the p-n junction in silicon electronics was established. In 1918, Czochralski, a Polish scientist, discovered a method for single crystalline silicon production, which enabled the production of monocrystalline solar cells in 1941. The modern solar cells was been developed by D. M. Chapin and C. S. Fuller in 1954 at Bell Labs using a solid-state semiconductor junction. Since the good quality silicon wafers can be produced in 1950s, the silicon electronics became the main source materials for PV industry. In 1979, after 7 years research, Dr. Ching W. Tang discovered the concerning the first organic cell and published his research results at 1986. In 1991, Grätzel and O’ Regan found the first dye-sensitized photovoltaic device which has efficiency in full sunlight of 7.1%. Since then, Perovskite materials have been first incorporation into a solar cell was reported by Miyasaka et al. in 2009, this cell was based on a dye-sensitized solar cell, and generated only 3.8% power conversion efficiency. A recent power conversion efficiency of 16% at AM 1.5G one sun illumination was reported, and the efficiency is expected to be beyond 20% in the near future. Over times, there were continuous in the increasing of conversion efficiency with respect to materials development. Figure 1.1 presents the efficiency of recorded best research solar cells performance, generated by National Centre for Photovoltaics in US. The Wiley publisher group also makes a reliable solar cell efficiency table every year.
Figure 1.2: Schematic representation of a silicon monocrystalline solar cell, the circles presents the exited electrons and holes.

For another classification in solar cells industry, the traditional silicon solar cells technique belongs to the first generation technologies. The first generation silicon solar cells use mono- or multi-crystalline silicon as the main materials for the production of solar cells. Figure 1.2 shows a typical monocrystalline silicon solar cell. This kind of silicon solar cells are a single-junction solar cell in different regions, n-type or p-type semi conducting materials are doped. The efficiency of these single junction solar cells can rise up 20%. The improvements of silicon single-junction solar cell were addressed by silicon heterojunction solar cell. Figure 1.3 shows a typical structure of silicon heterojunction solar cell. Although the efficiency of this kind of solar cell is relatively very high in comparison with that of organic solar cells, the high cost and the pollution causing in the production process setback the development of the PV industry.
Figure 1.3: Schematic diagram of a silicon heterojunction solar cell.

The second generation solar cells incorporate the thin film solar cells produce thinner layer crystals than the first generation materials film, made by depositing one or more thin layers, or thin film of photovoltaic material on a substrate, such as glass, plastic or metal. It was reported that using CdTe and CIGS (Copper Indium Gallium Selenide) thin film to generate a single junction solar cells, the efficiency of this thin film solar cells can raise up to 21%. However, since they involve a technically demanding of high requirement for producing process and it was found that it is very difficult to transfer this technology from laboratory scale to commercial scale products.

The third generation solar cells incorporate organic solar cells and several different types of dye sensitized solar cells and so on. The organic solar cells include Schottky-type solar cell, bi-layer heterojunction solar cell and bulk heterojunction solar cell (BHZ). The Schottky-type solar cells have a typical metal-organic-metal sandwich structure. From R. O. Loutfy and J. H. Sharp’s research, macrocyclic molecules such as porphyrins and phthalocyanines were considerable material choices for the organic layer present in the sandwich structure. In 1985, Tang et al first reported the bi-layer heterojunction solar cells. The efficiency of organic solar cell
was from then improved significantly. In his work, small molecules of copper phthalocyanine and a perylene tetracarboxylic derivative were used as the active layer of solar cell.\textsuperscript{11} However, the diffusion of excitons only occurs in several nanometers near the interface of two organic materials in the bi-layer heterojunction solar cell, which constituted one of the main limitations for the bi-layer heterojunction solar cell. In order to solve this problem, bulk heterojunction solar cell, which rely on the mixing of the electron donor and acceptor materials together was introduced.\textsuperscript{23, 24} Bulk heterojunction is an interpenetrating network of acceptor and donor where the phase separation is commonly between 10 nm and 20 nm, which is within the effective diffusion length of an exciton. The emergence of bulk heterojunction is a breakthrough in organic solar cell.

Another kind of third generation solar cell is the dye-sensitized photovoltaic device, which was firstly founded in 1991 by Grätzel and O'Regan.\textsuperscript{12} Dye-sensitised solar cell combines organic and inorganic components together and assembly nanomaterial together to build up a multilayer structure. The dye molecules are working as a light harvesting material in the cell structure to absorb photos and generate free electrons by the photovoltaic effect. Modern dye-sensitized solar cells are composed of a porous layer of titanium dioxide nanoparticles, covered with a molecular dye that absorbs sunlight. The titanium dioxide is immersed under an electrolyte solution, above which is a platinum-based catalyst. As in a conventional alkaline battery, titanium dioxide regarded as an anode and platinum regarded as a cathode are placed on either side of a liquid/solid electrolyte conductor.
Figure 1.4: (a) ABX$_3$ perovskite structure showing BX$_6$ octahedral and larger A cation occupied in cubo-octahedral site, X = oxygen, carbon, nitrogen or halogen; (b) Unit cell of cubic CH$_3$NH$_3$PbI$_3$ perovskite.$^{25}$

Perovskite solar cells are a recent discovery, where a solid-state material such as a perovskite was first used as light absorber.$^{13}$ Figure 1.4 presents a typical structure of perovskite. These are adaptations dye sensitized solar cells in technical terms limit use this cheap and available range of materials. The most commonly studied perovskite absorber is methylammonium lead trihalide (CH$_3$NH$_3$PbX$_3$, where X is a halogen ion such as I$^-$, Br$^-$, Cl$^-$), with a bandgap between 2.3 eV and 1.57 eV depending on halide content. It was first used as a replacement of the dye in dye-sensitized solar cells in order to solve the problem of limited light harvesting of organic dye.$^{13}$ However, the perovskite was found to easily dissolve or decompose in the liquid electrolyte, and it even degraded in a few minutes when it first designed. Solid state hole transporting conductor was then applied to solve the instability of perovskite. As of June 2014, the certified record a power conversion efficiency of 17.9% was achieved by the Korean Research Institute of Chemical Technology (KRICT), which was certified by the National Renewable Energy Laboratory (NREL).$^{25}$
1.1.3 Organic Bulk-heterojunction Solar Cells

Organic solar cells, as one of the most studied type of PVs to date are based on donor-acceptor heterojunctions and attract increasing interest due to the advantages of light weight, low cost and flexible as well as due to the fact that a vast range of materials with tuneable band gaps are available. Organic solar cells were firstly discovered due to the study of perylene-iodine complex in 1954. As described in previous section, the organic solar cell is limited by low dielectric constant of organic semiconductor, which leads to the slow mobility of electron and hole and the exiton diffusion length of charge carrier is significant limited. It is reported that the diffusion length of organic semiconductor is believed to be 5 nm to 20 nm. As a result, the thickness of phase separation and the active layer should be extremely carefully controlled.

The Schottky-type solar cells, first generation of organic solar cells, have a sandwich layered structure, which includes an organic semiconductor layer between the cathode and anode. In this type of solar cells, the built-in potential is highly relied on the electrodes properties, for instance, the work function of electrodes (or Schottky barrier) formed at the interface of metal electrodes and semiconductor. In 1986, a huge improvement in the organic solar cells technology was made due to the discovery of bi-layer heterojunction solar cells. In Tang’s work, small molecules of copper phthalocyanine and a perylene tetracarboxylic derivative were functionalised as active layer however only a 1% conversion efficiency was achieved. The bi-layer improves the efficiency of organic solar cells is majorly due to the enlarged interactive face between donor-acceptor system.

The discovery of Bulk heterojunction solar cell was firstly established by Yu and Halls et.al. Bulk heterojunction solar cells have an interpenetrating network of acceptor and donor where the phase separation is commonly between 10 nm and 20 nm, within which is the effective diffusion length of exciton. The development of bulk
heterojunction solar cells is a revolution in organic solar cells. Figure 1.5 shows structure of a bi-layer heterojunction solar cell and of a bulk heterojunction solar cell.

**Figure 1.5**: Typical organic solar cells devices based on donor–acceptor heterojunction architectures. The green materials represent to donor material and the red materials represent acceptor materials (a) bi-layer heterojunction solar cells configuration; (b) bulk heterojunction solar cells configuration; (c) fundamental electron transfer procession occurring within the energy levels of function donor and acceptor heterojunction layers in solar cells\(^{31}\).

As presented in Figure 1.5 and deliberated previously, the organic solar cells functionalised when an exciton is produced by absorption of light. The pair electron-hole bounded by Coulomb interaction must reach the junction and there it dissociates into two free charge carriers. The free charge-carrier transport and collection takes place at the external electrodes. Those excitons do not reach the interface recombine and do not contribute to the photocurrent which means that the smaller the diffusion length, the higher the chance the exciton can reach the junction. The improvements in bulk heterojunction solar cells constituted of tuning the distance between the blended donor and acceptor materials. When this is reduced into nanometre ranges, the interface between donor and acceptor materials is enhanced.
Thus, new forms of donor-accepter blended structures can improve the efficiency of PV.

In bulk heterojunction solar cells, the donors are typically organic systems having an electron rich structure, whilst the acceptor normally shows conjugated π bonds, which due to the electron affinity can be the active part with the role to transport electrons. Another important factor for donor-acceptor is the energy level of the donor and acceptor, which should be well matched. As a result, ideally, in organic bulk heterojunction solar cells, the LUMO of the donor systems should be at least 0.3-0.4 eV higher that the acceptor’s LUMO energy level, which is needed to address the efficient exciton dissociation. At the same time, the band gap between the donor’s HOMO energy level and the acceptor’s LUMO energy level should not be too large to become positive to electron exchange. The band gaps between donor HOMO energy level and the acceptor LUMO energy determine the open circuit voltage and a big energy gap can lead to an energy loss, causing a lower open circuit voltage for the resulting solar cell.
## Table 1.1 Small molecules used in organic solar cells

<table>
<thead>
<tr>
<th>Small molecule organic solar cells</th>
<th>Fullerene and its derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acceptor</td>
<td>Perylene Diimide and its derivatives</td>
</tr>
<tr>
<td>Non-fullerene</td>
<td>Pentacene and its derivatives</td>
</tr>
<tr>
<td></td>
<td>Vinazene and its derivatives</td>
</tr>
<tr>
<td>Donor</td>
<td>Diketopyrrolopyrrole(DPP) and its derivatives</td>
</tr>
<tr>
<td></td>
<td>Oligothiophenes(OT) and its derivatives</td>
</tr>
<tr>
<td></td>
<td>Triphenylamine (TPA) and its derivatives</td>
</tr>
<tr>
<td></td>
<td>Anthradithiophene and its derivatives</td>
</tr>
<tr>
<td>Acceptor/donor dyad</td>
<td>Oligo(p-phenylenevinylene)-fullerene</td>
</tr>
<tr>
<td></td>
<td>Zn-phthalocyanine-fullerene</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

In order to optimise the performance of the a selection of PVs, donor and acceptor materials combinations have been studied and tested so far.\(^{30}\) Compared with the use of polymers, small molecules were studied for bulk heterojunction solar cells assembly over a longer period of time, due to the following advantages: relatively easy to prepare and purify, and offer a significantly improved reproducibility.

More importantly, with advancement of supramolecular chemistry, the modification of small molecule of the classes listed in table 1.1 becomes accomplishable.\(^ {31}\) For instance, changing the variety or adding functional side groups became possible, which means the HOMO and LUMO energy level of small molecule can be easily tuned.

This modification is very important for bulk heterojunction solar cells production and design of other solar cells incorporates small molecule in their systems. It means that solar cells can be designed and optimised not only at the assembly stage, but from the started, though careful choice of the material. Small molecule can be classified by their working role in bulk heterojunction solar cells: donor, acceptor and acceptor/donor dyad, which can simultaneously function either as donor or acceptor depending on the environment. Table 1.1 shows the common small molecule used in organic solar cells.

As shown in Table 1.1 acceptor materials used in organic solar cells can be classified in two groups: one is fullerene and its derivatives, and the other one includes non-fullerene and functional derivatives. From the class of fullerene and its derivatives, PC\(_{71}\)BM, (molecule structure shown in Table 1.2) shows an impressive performance for its good electron mobility and solubility.

Recently, the research of acceptor dyad and triad systems based on perylene tetracarboxylic diimide and fullerenes also show promising properties.\(^ {32}\) For donor
Chapter 1 Introduction

materials, phthalocyanine (Pc) and its metalations present good property in light absorption and had been applied in first bi-layer structure. It was also reported by Uchida, a CuPc and C\textsubscript{60} homogeneous layer active layer correspond with a C\textsubscript{60} and 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline deposited cathode exhibits 3.5\% efficiency.\textsuperscript{33} Diketopyrrolopyrrole (DPP) and its derivatives donor materials also display good properties. A 4.4\% efficiency and 0.9 eV open circuit voltage was reported as using DPP (TBFu)\textsubscript{2} as donor and PCBM as acceptor.\textsuperscript{34} Recently, Zhang reported to use modified DPP in organic bulk heterojunction solar cells to enhance the hole mobility from $4.14 \times 10^{-4}$ to $7.75 \times 10^{-3}$ cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} and raises the fill factor from 27\% to 57\% when blended with PC71BM.\textsuperscript{35} Table 1.2 exhibits some of small molecules in organic bulk heterojunction solar cells.
**Table 1.2**: Small molecule used in organic solar cells and their structure.

<table>
<thead>
<tr>
<th>Types</th>
<th>OSCs structure</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-layer(^1)</td>
<td>ITO/CuPc/PV/Ag</td>
<td>CuPc</td>
<td>PV</td>
<td>1%</td>
</tr>
<tr>
<td>BHJ(^{33})</td>
<td>ITO/CuPc,(C_{60}) /(C_{60})/BCP/Ag</td>
<td>CuPc</td>
<td>(C_{60})</td>
<td>3.5%</td>
</tr>
<tr>
<td>BHJ(^{36})</td>
<td>ITO/PEDOT:PSS/m-MTDATA/ZnPc, (C_{60})/n-MPP/Al</td>
<td>ZnPc</td>
<td>(C_{60})</td>
<td>3.37%</td>
</tr>
<tr>
<td>BHJ(^{37})</td>
<td>ITO/MoOx/DTS(PTTh(_2)(<em>2),PC(</em>{70})BM/Al</td>
<td>DTS(PTTh(_2)(_2))</td>
<td>PC(_{71})BM</td>
<td>6.67%</td>
</tr>
<tr>
<td>BHJ(^{34})</td>
<td>ITO/DPP(TPFu)(_2),P CBM /PEDOT:PSS/Al</td>
<td>DPP(TBFu)(_2)</td>
<td>PC(_{71})BM</td>
<td>4.4%</td>
</tr>
<tr>
<td>BHJ(^{35})</td>
<td>ITO/PEDOT/BDB, PCBM/Al</td>
<td>BDB</td>
<td>PC(_{71})BM</td>
<td>0.91%</td>
</tr>
</tbody>
</table>
1.1.4 Dye-sensitised solar cells (DSSCs)

Dye-sensitised solar cells (DSSCs) are widely studied and longstanding candidates for the current and next generation of solar cells. As mentioned above, although it was Edmund Bequerel who discovered the photovoltaic effect (which describes the conversion of sunlight into electricity) it was not until 1991 when Grätzel and O'Regan reported the first modern dye-sensitized photovoltaic device thus introduced a mesoporous semiconductor electrode with a high internal surface area which should be a efficiency in full sunlight of 7.1%. This discovery led to a paradigm shift in the fields of photoelectrochemistry and photovoltaics in general. Before the report on Grätzel and O'Regan work, previous efforts to develop dye-sensitized solar cells all failed due to the fact that there was no smooth semiconductor surface introduced, specifically that of the TiO$_2$ thin film, in the system. In 2006, Y. Chiba et al. reported a DSSC with a efficiency of 11.1%. A typical DSSC includes four major components: photodelectrode, dye molecule, electrolyte counter electrode, and a typical representation of the DSSC is shown in Figure 1.3.

Compared with other type of solar cells, the DSSCs have several different advantages. First of all, the cost of manufacturing a DSSC is relatively low since these combine simple synthetically available organic and inorganic components, which are assembled on the nanoscale leading to the build-up of complicated hybrid structures. Additionally, the fabrication process of DSSCs is relatively simple compared with conventional p-n semiconductor solar cells, where electron-hole pairs are generated in the bulk material and then there is a need for these to diffuse to the p-n interface in order to be extracted. The charge generation in DSSCs only takes place at the material surface, as a result, the requirement for material purity is dramatically reduced. Furthermore, the fabrication process is relatively simple despite the need for specialised equipment, it does not require a high vacuum, ultrahigh temperatures and processing in a cleanroom. Due to their layered structure, the DSSCs can be
generated by using printing technique, which makes them accessible to industrial scale generation of such device.\textsuperscript{42}

![Schematic representation showing the operating principles and energy level diagrams in a typical dye-sensitised solar cell.\textsuperscript{43}](image)

**Figure 1.6:** Schematic representation showing the operating principles and energy level diagrams in a typical dye-sensitised solar cell.\textsuperscript{43}

The operating principles of DSSCs rely on the following processes, described in the equation (1)-(5) below: (1) dye molecule photoexcitation, (2) electron ejection, (3) regeneration of dye molecule with electrolyte, (4) recombination of TiO\textsubscript{2} and (5) regeneration of electrolyte. Figure 1.3 also contains a sketch of a typical energy transfer progress and operating principles above occurring in DSSCs.

The dye molecule (referred to D) as following, absorbs light \((h\nu)\) and leads to the formation of its electronically excited state (denoted D*):

\[
D + h\nu = D^* \quad \text{(Eq. 1: Photoexcitation)}
\]

The excited state molecule D* can then decay back to the ground state by undergoing relaxation or inject the electron to the conduction band TiO\textsubscript{2}
\[ D^* = D + h\nu \quad \text{(Eq. 2: Relaxation)} \]
\[ D^* = D^+ + e^- \quad \text{(Eq. 2: TiO}_2\text{ charge injection)} \]

After injection, the electron can transfer through the mesoporous network of TiO\textsubscript{2} and reach the back-collector electrode to contact with external circuit. The oxidised dye molecule then reduces rapidly to the ground state by interacting with electrolyte (normally I\textsubscript{3}, but can consist of different anions, depending on the nature of DSSCs).

\[ 2D^+ + 3I^- = 2D + I_3^- \quad \text{(Eq. 3: Regeneration of dye)} \]

In the absence of a redox mediator and due to a rapid reduction process of the dye molecule, this can recombine with the electron from TiO\textsubscript{2} and the process ends with no photocurrent. This situation can also occur with an inefficient I\textsubscript{3} regeneration process.

\[ D^+ + e^- (\text{TiO}_2) = D \quad \text{(Eq. 4: Recombination)} \]

The photocurrent electrons generated reaches the counter electrode through the external circuit and reduce I\textsubscript{i}. As a result, the entire energy transportation involving the dye molecule photoexcitation and electrolyte redox can be described as:

\[ I_3^- + 2e^- = 3I^- \quad \text{(Eq. 5: Regeneration of I)} \]

The overall effect of irradiation with sunlight is to drive the electrons though the external circuit and the DSSCs start to function.

As described above, the function of each working section can be reflected by
the operating principles (1)-(5). One of the more commonly used wide-gap semiconductor for DSSCs photoelectrodes is TiO$_2$ due to the fact that this is a material which stable, nontoxic and has an energy gap of ~3.0eV.

An important requirement for the photoelectrode semiconductor is a high transport mobility of the charge carrier, which in needed to reduce the electron-transport resistance.$^{39}$ As an alternative, ZnO having different nanostructures has been actively been studied in this context due to its similar bandgap and conduction band edge.$^{44,45,46}$ Yang et al. also reported a dense array of oriented crystalline ZnO nanowires with a surface area up to one-fifth of that of TiO$_2$, which had a sun conversion efficiency of 1.5 %.$^{47}$ Compared to similar ZnO-based devices with power efficiency up to 1.6 %, ZnO nanotube based cells showed exceptional photovoltage, but the higher surface area may absorb excess dye molecules.$^{48}$ Besides ZnO, some other binary metal oxides, such as Fe$_2$O$_3$, ZrO$_2$, Nb$_2$O$_5$, Al$_2$O$_3$, and CeO$_2$, and ternary compounds, such as SrTiO$_3$ and Zn$_2$SnO$_4$, have been also studied and tested as photoelectrodes in DSSC, but their efficiency is significantly lower with respect to that of TiO$_2$.

Along with the photoelectrode, a key component of the DSSC is the photosensitisier, a dye molecule, which functions as a light absorber and injects electrons into the conduction band of the photoelectrodes.

To be regarded as a competitive dye sensitiser, a molecule should have good solubility in a range of organic solvents, strong light absorption in the visible and near-IR region,

The photosensitisier should have anchoring groups, such as -COOH, -H$_2$PO$_3$, -SO$_3$H, their role is to bind the dye strongly onto the semiconductor surface. The dye of choice must have good thermal stability and good chemical stability and more
importantly, it should also have suitable HOMO and LUMO energy levels to match with other molecular components used in the same DSSCs. The dye molecule design is made that it does not favour its self-stacking/self-aggregation. It was also reported that through optimization of the molecular structure of the dye or by addition of co-absorbers that prevent aggregation, the unfavourable dye aggregation on the semiconductor surface could be avoided and the cell performance can be improved.\textsuperscript{39}

![Molecule structure of dye molecule N3 and N719.](image)

**Figure 1.4:** Molecule structure of dye molecule N3 and N719.

According to current reports, coordination complexes of Ru and Os supported by squaraines, porphyrins, phthalocyanines, perylenes, pentacene, cyanines, and coumarins can be used as competitive dye molecules.\textsuperscript{50} It was reported that the most efficient (>10\%) DSSCs incorporate the ruthenium polypyridyl complex N3 and a similar structure slat (Bu$_4$N)$_2$[Ru(4-carboxy,4-carboxylato-2,2-bipyridine)$_2$(NCS)$_2$] (N719).\textsuperscript{40,51} However, ruthenium is toxic and in low abundance on Earth. Furthermore, ruthenium based-dye molecules are not sustainable options likely to afford the large scale solar cells development in the long term. As stated above, some other type of small organic dyes molecule have also been tested in DSSCs: 9 \% efficient with indoline\textsuperscript{52}; 6.5 \% efficient with coumarin\textsuperscript{53}; 5.2 \% efficient with hemicyanine\textsuperscript{54}; 4.5 \% efficient with squarine\textsuperscript{55}; 7.1 \% efficient with porphyrin\textsuperscript{56}; 3.5 \% efficient with phthalocyanine\textsuperscript{57}. Rather than changing the type of the supporting ligand and molecule, the substitution of the coordinating metal centre has also been used in dye molecule optimisation.\textsuperscript{50}
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As another electron transfer part, the electrolyte plays a very important role in the DSSCs by facilitating the transport of charge between the dye molecule and the counter electrodes. The ideal liquid phase electrolyte and their solution should have low viscosity, negligible vapour pressure, high boiling point and high dielectric properties. Additional, factors like robustness, environmental sustainability and ease of processing also need to be considered prior to DSSCs industrial fabrication. As initially observed by Grätzel for his systems, all reports of efficient DSSCs to date (>4% at 1 sun illumination) have utilised the I$_3^-$/$I^-$ couple as the redox shuttle of choice. The good performance of I$_3^-$/$I^-$ in these cells was due to the attribution of efficient dye regeneration combined with exceedingly slow electron transfer from TiO$_2$ to I$_3^-$. For example, when I$_3^-$/$I^-$ was employed with compound N3, the regeneration yield was found to be quantitative. In addition, loss of electrons via interception by I$_3^-$ is at short-circuit and can be negligible, which allowed photo-injected electrons to be collected with near unity efficiency.58 Other attempts were also made to find an alternative redox system in DSSCs, for instance Br$_3^-$/Br$^-$,59 Co(II)/Co(III),60 Fe$^{2+}$/Fe$^{3+}$,61 triethanolamines,62 two pseudohalogen couples, (SeCN)$_2$/SeCN$^-$ and (SCN)$_2$/SCN$^-$,63 and other mixed systems of redox couples. Water-based electrolytes for dye-sensitized solar cells have also been investigated.64,65
Figure 1.5: Historic evolution from DSSC to recently updated perovskite solar cell$^{15}$.

As the generation of solar cells developed both from the perspectives of theory and fabrication techniques, the structural improvement of DSSCs benefited from some emerging new ideas of cell design. As shown in Figure 1.5, the evolution of the solar cell technology, form the original idea of the electrolyte-based mesoscopic DSSC (introduced by Grätzel and O'Regan), and after the attempts of replacing the electrolyte with an organic p-type hole conductor, solid-state DSSCs (ssDSSC) was emerged.$^{66,67}$ The extremely thin absorbers (ETA) cell as introduced as the dye molecule is replaced with a semiconductor layer.$^{68,69}$ For the *meso*-superstructured solar cell (MSSC), the ETA layer was replaced by a perovskite absorber and the n-type TiO$_2$ layer was replaced with a porous insulating scaffold.$^{70}$

As stated above, the perovskite solar cells and DSSCs are following the similar operating principles but they differ in terms of choice of materials and
structure. From a recent review by Henry J. Snaith\textsuperscript{15}, three future directions for the DSSCs and perovskite solar cells technology were proposed: firstly, the Al\textsubscript{2}O\textsubscript{3} could be removed but the perovskite is directly structured to give a porous film which can be subsequently filled with a charge conductor, giving a porous perovskite distributed p–n heterojunction solar cells. Secondly, thin-film p–i–n perovskite solar cells could be addressed, where no porosity is required and the device takes on an intrinsic or ambipolar structure where a thin perovskite film is sandwiched between p- and n type charge-extracting contacts. The third possibility includes, semiconductor MSSCs, where any solution-processed semiconductor, such as SbS\textsuperscript{71} can be structured by the porous scaffold to deliver the \textit{meso}-superstructured materials. These systems are all currently processed in parallel with current developments in DSSCs.

1.1.5 Summary to sustainable energy

In summary, solar energy and related sustainable technologies should and could play more important roles in societal daily life in the near future. Organic solar cells exhibit great promise for the future of photovoltaics, due to their high versatility and accessibility among different types of solar cell fabrication techniques. For organic solar cells, small molecules can be employed as the light absorber this has been demonstrated for both organic bulk heterojunction solar cells and for dye sensitised solar cells. Although the cells discussed above all differ in structure, the basic operating principle of BHJs and DSSCs is largely the same: the light absorber work as “donor”, which absorbs light and generate exited electrons, afterwards the electrons are transferred to “acceptor” and then transferred to an external current.

It can be seen from above discussions, either in the developments of bulk heterojunction solar cells, or due to the recent revolutions leading the photovoltaics development from DSSCs to perovskite solar cells and from perovskite solar cells to further proposed developing directions that almost all attempted efforts are based on synthesising and characterising new donor/accepter materials and improving the
electron diffusion efficiency within the systems. Thus, this study is aiming to address current difficulties wishing a small molecule-based donor incorporating a porphyrin motif and generative of a nanoscale material based acceptor system. These may be of relevance to future application in bulk heterojunction solar cells or dye sensitised solar cells structures.

1.2 Introduction of Porphyrins

1.2.1 Porphyrin motif as organic dye

One of the most attractive strategies is the development dye molecules in organic solar cells, given that these mimic natural photosynthesis processes in the conversion and storage of solar energy. As chosen by Nature, chlorophylls in plants function as antennae specifically designed to harvest light for the conversion of solar energy in complicated photosynthetic processes. Inspired by natural photosynthesis, scientists already utilised artificial chlorophylls model components, the porphyrins, as efficient light harvesting centres due to its capability to absorb light and convert to electric energy in solar cells.72

Porphyrins are a group of heterocyclic macrocycle organic compounds, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH−). The porphyrin macrocycle rings have a rich redox chemistry and highly delocalised π-electron system, this structure makes porphyrin useful in both photosynthesis and respiration.72

For photochemistry applications, porphyrin has a high electronic excitation energy, normally exceeding 2 eV, and this can power a strong electron transfer process, which is essentially the main reason behind the fact that porphyrins have good conversion between light and chemical/electrical energy.73 The application of porphyrins as solar cells materials though their role as dye molecules because of their strong Soret band in the 400 nm - 450 nm region, as well as the Q-band in the 500 nm
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- 700 nm region.\textsuperscript{74} Beside the strong light absorption properties, porphyrin molecules also present light photochemical and electrochemical stabilities as well as potential control of their redox potentials following the incorporation of different metal centre.\textsuperscript{75} Porphyrin molecule also exhibit appropriate LUMO and HOMO energy levels allowing them to act as panchromatic photosensitizers. Several studies have demonstrated that porphyrin dyes can show efficient photoinduced electron injection from their LUMO (lowest unoccupied molecular orbital) into the conduction band of TiO\textsubscript{2},\textsuperscript{76,77,78} and have a HOMO (highest occupied molecular orbital) energy level that lies below that of the redox couple in the electrolyte solution, required for the charge separation to take place.\textsuperscript{79} All above properties render porphyrin ligands as promising candidates in organic solar cells which allow them to act as “donor” molecule in DSSCs.

Figure 1.6 highlights the fact that these are three main kinds of light harvesting dye molecules and their recorded DSSCs efficiency. It can be seen from the graph that ruthenium-based sensitisers, which were first developed as dye molecules show high power convert efficiency, reported at around 10% - 11%. However, due to the toxicity and availability in low abundance on Earth, the ruthenium-based sensitisers are not suited for large scale fabrication, and are not deemed environmental friendly. The efficiencies of metal-free organic dyes were reported to be 9% to 10% during recent five years, whereby the best-performed organic dye is C219, reaching $\eta = 10.3\%$.\textsuperscript{80} But, the trend in the performance progress of metal-free organic sensitizers seems to have reached a bottleneck for their further development and there was no breakthrough discovery following on once thus direction has been proposed.
Figure 1.6 (a) Efficiency progressing records of DSSC from 1991 to 2012 on the basis of three representative sensitzers Ru-based complexes, organic dyes and porphyrin dyes\textsuperscript{81}. (b) Molecule structure of C219 dye molecule.
### Table 1.3: Porphyrin molecules used in some DSSCs which obtain high efficiency.

<table>
<thead>
<tr>
<th>Types</th>
<th>Dye molecules</th>
<th>Photoelectrode</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSCs$^{82}$</td>
<td><img src="image1" alt="Zn-1a" /></td>
<td>TiO$_2$</td>
<td>4.8%</td>
</tr>
<tr>
<td>DSSCs$^{83}$</td>
<td><img src="image2" alt="Zn-3" /></td>
<td>TiO$_2$</td>
<td>5.6%</td>
</tr>
<tr>
<td>DSSCs$^{56}$</td>
<td><img src="image3" alt="GD2" /></td>
<td>TiO$_2$</td>
<td>7.1%</td>
</tr>
<tr>
<td>DSSCs$^{84}$</td>
<td><img src="image4" alt="tda-2b-bd-Zn" /></td>
<td>TiO$_2$</td>
<td>7.5%</td>
</tr>
<tr>
<td>DSSCs$^{85}$</td>
<td><img src="image5" alt="YD2" /></td>
<td>TiO$_2$</td>
<td>11%</td>
</tr>
<tr>
<td>DSSCs$^{86}$</td>
<td><img src="image6" alt="YD2-oC8" /></td>
<td>TiO$_2$</td>
<td>12.3%</td>
</tr>
</tbody>
</table>

Note: The mentioned DSSCs are co-sensitized with another organic dye.
Table 1.3 shows some of the porphyrin molecules that have been applied in recent years and the cell power conversion efficiency. Together with figure 1.6, it can be seen that recent porphyrin based DSSCs development showing a promising advance with the progress curve. Porphyrin molecule applied as dye molecule in DSSCs was pioneering reported by Kay and Grätzel, a mesoporphyrin IX dye was used and achieved a 2.6%. From then, there was no breaking research released, until 2004, Md. K. Nazeeruddin reported by using a Zinc centre porphyrin, correspond to Zn-1a in table 1.3, the DSSCs efficiency can rise up to 4.6%. Followed by their work, by applying Zn-3, Q. Wang and co-workers reported a DSSCs with a 5.6% efficiency. In 2007, the same group reported porphyrin sensitisers in another series, in which porphyrin GD2 in table 1.3 exhibits a 7.1% efficiency. As reaching at 7.1% efficiency, porphyrins work as dye molecules in DSSCs could compete with organic small molecule even ruthenium sensitisers and open a great opportunity to enhance the efficiency by modifying their structure. In 2009, Kim and co-workers reported a Zinc porphyrin (td-2b-bd-Zn) with a diarylamino group and reached an efficiency of 7.5%. More excitingly, Yeh and Diau reported YD2 porphyrin with two long alkyl chains to improve the thermal and photochemical stability and obtain 11% efficiency. Grätzel and co-workers reported an optimised performance DSSCs by using YD2-oC8 and a co-sensitised organic dye Y123, this cells efficiency can up to 13.1%, the reason for this promising improvement is due to the upward shift of the TiO\textsubscript{2} conduction band and the enhanced electron lifetime. The long alkoxy chains play an essential role to diminish the degree of porphyrin dye molecule aggregation.

As described above, the development of cells efficiency goes alone with the porphyrin molecule modification. A very obvious modification method for the porphyrin molecule is to convert the free base porphyrin into metallloporphyrin. Both experimental results and computer simulations have demonstrate that by adding a meter centre, the absorption behaviours of porphyrin can be varied. Zinc porphyrin molecules were the most common and widely used dye molecule in DSSCs
due to the low cost and being nontoxic. Alongside metalation of the porphyrin core, the substitution of groups on the porphyrin can also allow tuning of the absorption the wavelengths, tailing of molar absorption coefficient, as a result of the HOMO/LUMO energy level modifications. As a result, grafting different groups around porphyrin ring have become one of the main pathways to improve electrochemical properties of porphyrins, and thus improve the efficiency of DSSCs.

Functionalisation and modification of the porphyrin ligand have been carried out to overcome the problems occurring porphyrins were employed as dye molecules in a DSSCs. Porphyrins are highly conjugated and planar systems, which means the porphyrin have an inherent tendency to self-aggregate in solution at high concentrations. As stated above, the dipole/dipole interactions allow a rapid migration of the excited state between neighbouring dye molecules and this could lead to the annihilation of excitons, which to turn dramatically decrease the dye efficiency. Thus, the modification of the porphyrin ligand should not allow a high level of aggregation to occur. To date, it is generally accepted that the laboratory scale synthesis of the porphyrins is more challenging than that of most other dye molecules under investigation for DSSCs. The main reason is still due to the high aggregation trends but also due to purification issues, as the solubility in most organic solvent is similar for the starting materials, intermediates and final product. The flexibility in the synthesis of metalloporphyrins is introduced as much cheaper metals such as iron and zinc can be incorporated, which then contributes to the tuneable absorption wavelengths and a tuneable π-electron network. By altering the functional groups around the porphyrin it is possible to alter the π-electron density on the ligand plane, which is then beneficial to the interactions of porphyrins and its versatility in engaging in donor-acceptor interactions are supramolecular systems formation.

Therefore, the strategy of modifying porphyrin molecules by introducing new functional groups around porphyrin was of interest recently. Porphyrin-based hybrid
systems are able to avoid self-aggregation and capable of altering electron density and the injection pathway are of interest in DSSCs design.

![Figure 1.7](image)

**Figure 1.7:** Typical structure of a free base porphyrin plane presenting meso-position and β-position which may be functionalised in addition to the 2H available for exchange with a metal centre.

As shown in Figure 1.7, there are two types of positions in the porphyrin molecule that can be used for molecule modification: the four meso-positions and eight β-positions. By introducing functional group at the β-position the resulting system can have an enhanced capability of electronic coupling of the dye with the surface of TiO₂. This concept, to design β-functionalized porphyrin sensitizers, was initially explored by Kim and co-workers. They demonstrated that Zinc(II) porphyrin (2b-bdta-Zn, shown in table 1.3) with two equivalent π-conjugated malonic-acid linkers effectively enhanced the efficiency of electron injection and retarded the charge recombination. While the substituted linkers at the four meso-positions of the porphyrin have been used to suppress dye aggregation, the porphyrin YD2 (presented as table 1.3) represented an attractive example of a meso-position modification. The functional groups introduced can be either highly conjugated groups or long alkoxy chains. The long alkoxy chains in porphyrins play an important role towards diminishing effectively the degree of dye aggregation, which is crucial for an improved device performance since they generate interspace in
In summary, both meso-position and β-positon linkage modifications of the porphyrin core can lead to efficient improvements of dye molecule towards DSSCs applications. But, regardless of precise positions and choice of functional groups, the role of those modifications needs to overcome the problem of self-aggregation and enhance the electron injection properties when employing porphyrins as dye molecules in DSSCs. In this project, a serious of modified, functionalised porphyrins including of the groups at both the meso-position and β-positons (e.g. conjugated groups, and long alkyl chains) were synthesised on a laboratory scale aiming to improve understand the challenges in the use of these dye molecules in PVs.

1.2.2 Interactions between within porphyrin molecules and carbon nanomaterials

As stated above, fullerenes are suitable systems acting as electron-acceptor materials of relevance to organic solar cells, due to their capability of acting as highly efficient electron-transfer reduction media. In some type of organic solar cells, the efficient induced electron transfer occurs at the interface between donor molecule and the fullerene layer interface. While porphyrins can be regarded as one of the most efficient dye molecules in DSSCs due to present remarkable light harvesting ability, as discussed above, their application in the presence of fullerenes, giving rise to donor and acceptor complex systems seems ideal as an approach in solar cells applications. Figure 1.8 shows an example of fullerene porphyrin complex and their supramolecular assembly.
Figure 1.8: Crystal structures of tubular assemblies of a $C_{60} \subset \text{Ni}_{2}\text{CPDPy}$ donor-acceptor complex. Hydrogen atoms are omitted for clarity: (a) side view; (b) top view.\textsuperscript{95}

Porphyrins and fullerenes are known to form supramolecular complexes, which contain close contacts between one of the electron-rich module led ring bonds of the guest fullerene acting as a “donor” and the molecule of the host porphyrin acting as a “host”.\textsuperscript{96, 97, 98, 99, 100} The contact distances in porphyrins and $C_{60}$ are of the order of 2.7 – 3.0 Å, which is much longer than normal metal–olefin bonding distances commonly found in organometallic complexes.\textsuperscript{96} The porphyrin–fullerene interaction energies are reported to be in the range from −16 to −18 kcal mol\textsuperscript{−1},\textsuperscript{101} which is a very strong force capable of driving the formation of porphyrin and $C_{60}$ supramolecular complexes. The interactions between porphyrin and fullerene can be explained by π-π interaction involving van der Waals forces.\textsuperscript{102} But, it is worth noticing that in a study by Reed, a free base porphyrin was found to bind to a fullerene exhibiting a more strong link than metalloporphyrins and a suggested
explanation was due to the importance of electrostatic interactions involved.\textsuperscript{100} The non-covalently binding and hydrogen bonding allow the charge transfer without disruption of the $\pi$-system. Also, no additional input energy is required at the formation of such hybrids. In some cases, the metal centre in the metalloporphyrin can be linked with $\text{C}_{60}$ in a combination with metal ligand coordination interaction. An example shown in Figure 1.9 and this linking strategy also provides a novel non-covalently bonding type in fullerene-porphyrin complex design.

\textbf{Figure 1.9}: A supramolecular fullerene-containing diad, the donor-acceptor components are brought in close proximity by metal–ligand interactions.\textsuperscript{103}

The functionalised Zn(II)-porphyrins of interest for this project have been isolated on an analytical scale for Dynamic combinational chemistry studies. Dynamic combinatorial chemistry methods were also applied to generate new compounds held together by fullerene and porphyrin donor-accepter interactions. Dynamic combinatorial chemistry relies on the molecular recognition, and is a new approach to synthesise molecules and their complexes on an analytical scale.\textsuperscript{104} Dynamic combinatorial libraries were carried out by linking simple building blocks together with a reversible reaction under thermodynamic control. The libraries are allowing a constant interchange of building blocks resulting in a mixture of library members in equilibrium.\textsuperscript{104} In fullerene and porphyrin system, the dynamic combinational concept was applied by regarding a porphyrin dimer as receptor and
fullerene as a guest. Amy L. Kieran reported several approaches in porphyrin and fullerene dynamic combinatorial chemistry, but the limitation of that work was the tiny scale on which the new compounds were isolated.\textsuperscript{105,106} Figure 1.10 is an example presenting the dynamic combinatorial chemistry of a porphyrin species using small molecule templates to recognise the dimer from the mixture.

**Figure 1.10:** Binding of guests inside the adjustable porphyrin dimer receptors\textsuperscript{105}.

The combination of fullerene and porphyrins can also be addressed by covalently linking such molecules.\textsuperscript{107,108,109} The covalent binding or the donor and the acceptor allows the orientation and distances between porphyrin and fullerene to be designed in advance. In the covalently linked complexes, highly conjugated linking groups are employed to allow for an efficient electron transfer, but this change can alter the π-electron system in both the porphyrin and the fullerene systems.

It has been shown that complexes incorporating a fullerene and a porphyrin
show great promise as synthetic scaffolds for new functional materials for photovoltaic applications but due to the synthetic challenges so far, only few investigations into the device fabrication based on porphyrin oligomers and carbon nanotubes or graphene/graphene oxide could be carried out.\textsuperscript{110} It is known that, from the class of carbon-based nanomaterials, carbon nanotubes and graphene/graphene oxides also have promising electronic and mechanical properties in their own right, which makes them even more interesting when combined with porphyrin molecules as the resulting nanohybrids can act as a donor and acceptor system. Nakashima first reported that a complex formed by a porphyrin and single walled carbon nanotubes via non-covalent interactions.\textsuperscript{110} After this study, some research has been carried out in this area: Raghu Chitta reported a Zinc(II)-porphyrin non-covalently linked to single-walled carbon nanotubes and showed that these synthesis are held together by \(\pi-\pi\) interactions.\textsuperscript{111} The covalent linking strategies were investigated to an even more limited extent: Zhen Guo reported a method to covalently link porphyrin with SWNTs by a diazonium group.\textsuperscript{112} Similar reactions were carried out between graphene/graphene oxides with a porphyrin substrate. Nikolaos Karousis reported a covalently linked porphyrin with graphene by diazonium group, as a direct adaptable converting from Zhen Guo’s research.\textsuperscript{113} In 2012, Murali Krishna reported a covalently linked porphyrin and graphene oxide with metal or metal free porphyrin by using the defects group on the edge of graphene oxide.\textsuperscript{114}

Thus, in the project, we will investigate new modes of assembling between carbon nanomaterials and porphyrins. These showed great promise as new synthetic scaffolds for functional materials for photovoltaic applications.\textsuperscript{115} Our new nanohybrids have been designed to incorporate with SWNTs and graphene/graphene oxide, and explore by both supramolecular self-assembly method (which typically leads to the \(\pi\)-system of the carbon nanomaterials to remain unaltered) and a more synthetically demanding route, which living an covalent approach to link the donor and accepter (but disruptive for the experimental aromatic synthesis).
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1.3 Carbon nanomaterials

1.3.1 Introduction to carbon nanotubes

Figure 1.11: schematic representation of the relationship of C\textsubscript{60}, SWNTs and graphite consists with several single-layer graphene sheet\textsuperscript{116}.

As one of the most abundant elements on the planet, carbon is the \textit{materia prima} for life and the basis of all organic chemistry. Graphite, diamond and amorphous carbon are the best known natural allotropes of carbon, but several other man made materials emerged over the last 25 years such as fullerene, carbon nanotubes, and graphene. The carbon atom in graphite presents a non-crystalline, irregular and glassy state. Graphite consists of layers of graphene stack together to form a 3-D structure. Graphene is made out of carbon atoms arranged on a honeycomb structure made out of hexagons, and can be thought of as composed of benzene rings stripped out from their hydrogen atoms.\textsuperscript{117} Diamond holds an sp\textsuperscript{3} hybridised and each of the carbon atoms was forced to attach with other four carbon atoms in a tetrahedral arrangement, then three other tetrahedral structures are joined to form a 3-D six member rings structure.
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Other than the naturally formed carbon allotropes, human made carbon allotropes also presented promising properties. Fullerenes, regarded as zero-dimensional materials, are the molecules where carbon atoms are arranged spherically and carbon atoms in this molecule fill the sp² orbital. Recently, Andrey Chuvilin et al. directly visualized a process of fullerene formation from a graphene sheet using aberration-corrected transmission electron microscopy. Carbon nanotubes can be regarded as by rolling graphene sheet along a certain direction and then relinking the carbon bonds. Thus, carbon nanotubes can vary in length and be thought of as one-dimensional material. Figure 1.11 is a schematic representation of the relationship of C₆₀ and SWNTs with graphene.

The discovery of carbon nanotubes were converted from of C₆₀. The synthesis of multi-walled carbon nanotubes (MWNTs) was firstly reported by Iijima in 1991, as a result of an experiment where he pursued the synthesis of fullerenes via arc discharge method. After further study, single-walled carbon nanotubes (SWNTs) were then reported in 1993, and a method was specifically designed to produce such higher fullerenes by adding transition-metal catalysts (for example Ni and Y) to the graphite in an arc discharge method. Since then carbon nanotubes have been extensively considered for applications in many different research fields, due to their structural, physical and electronic properties such as high chemical and thermal stability, high elasticity, tensile strength, metallic conductivity and large surface area. SWNTs have diameters 0.5 nm to 5 nm (commonly around 1 nm to 2 nm), whereas the diameter of MWNTs are 2 nm to 100 nm (commonly around 10 nm). The lengths of carbon nanotubes are typically in the micrometres range, but in some reports it has been shown that these can be up to millimetres or even centimetres. The inner space of carbon nanotubes, which are encapsulated, employed as a nano-reactor, to capable monitor or control the reactivity of fullerene and other small molecules to form some unusual supramolecular and covalent structures.
Figure 1.12: The rolling of a graphene form a single-walled carbon nanotube \((n, m)\) structure is formed by sheet. This is formed along the chiral vector \(C=n\mathbf{a}_1+m\mathbf{a}_2\), \(\mathbf{a}_1, \mathbf{a}_2\) are the graphene lattice vector (double bonds have been removed for clarity)\(^{125}\).

The structure of SWNTs can be regarded as that formed by rolling a graphene sheet (or single layer of hexagonally linked carbon atom) by a specified vector \(C\), which in term of a set of two integers \((n, m)\) corresponds to graphene vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\), (as it is show in Figure 1.12). The chiral vector \(C\) is used to represent the overall chirality of the SWNTs and can be presented by equation:

\[
C=n\mathbf{a}_1+m\mathbf{a}_2
\]

The pair of integers \(n\) and \(m\) can be used to define the unit chiral vector and also to calculate the diameter of the SWNTs:

\[
d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi}
\]

Where the parameter \(a = 1.42 \times \sqrt{3}\) Å corresponds to the lattice constant in the graphite sheet. According to the chirality, the SWNTs can be classified as three types: Zigzag, (where the integer appears as \((n, 0)\)), Armchair, (where the integer is \((n, n)\)) and chiral, (where the integer \(m\) is any number between 0 and \(n\)). Figure 1.13
shows a schematic diagram of a fragment of a (6,6) armchair SWNTs and that of a (10,0) zigzag SWNTs.

Figure 1.13: Schematic representation of (6,6) armchair SWNTs and (10,0) zigzag SWNTs fragments.

In a similar way, the structure of nanotube could also be represented by using a chiral angle $\theta$, the following equations define the structures:

$$\theta = \tan^{-1} \left( \frac{\sqrt{3}m}{m+2n} \right)$$

According to the equation above, in armchair structure SWTNs, where $m = n$, thus: $\theta = \tan^{-1} \left( \frac{1}{\sqrt{3}} \right) = 30^\circ$; while in zigzag structure SWNTs, where $m = 0$, $\theta = \tan^{-1}[0]=0^\circ$; and in chiral structure SWNTs, $0 < m < n$, thus $0^\circ < \theta < 30^\circ$

For SWNTs, the chirality of the tube structure not only gives an account of their structural information, but also reflects the electric, optical, thermal, magnetic and mechanical properties of carbon nanotubes. For electrical properties, the conductivity of SWNTs can be calculated with the value of $n$ and $m$: for $n - m = 3q$, where $q$ is an integer, the structure of SWNTs is metallic, otherwise it is a semi-conductor. Therefore, for an armchair structure $(n, n)$, $q = 0$, hence all armchair
structured SWNTs were metallic. For chiral SWNTs, \( q = \frac{n-m}{3} \) and for zigzag SWNTs, \( q = \frac{n}{3} \), therefore the conductivity of those tubes varies depending on the calculation result and it was found that in predicting the majority of those SWNTs (found in such samples) were semi-conductive.\(^{122}\)

### 1.3.1.1 Synthesis of carbon nanotubes

The generation of carbon nanotubes involve several methods, but the most common method leading to high yield production of these materials include electric arc growth, laser growth and catalytic vapour deposition (CVD). Some of these methods are discussed briefly below.

**Electric Arc Growth** The electric arc growth is the earliest reported method to prepare carbon nanotubes. R. Bacon first introduce this method in carbon fibre generation.\(^{126}\) After this in 1990, Krätschmer and Huffman adapted this method towards fullerene generation in 1990.\(^{127}\) Iijima thereafter reported an adaption method for the fabrication of MWNTs and SWNTs. In the electric arc growth method, a high electric current, normally round 50-150 A, is passed through graphite electrodes under an inert atmosphere, for example 0.5 bar helium or argon. The inert gas atmosphere is used to protect the carbon source from reacting rapidly with oxygen and, at the same time, to control the inner pressure. As a consequence, the carbon source on the anode can be evaporated and then deposited on the cathode to from MWNTs. Electric arc growth can also apply in SWNTs synthesis by adding a metal catalyst, for instance Ni, Y, Fe or Co.\(^{128}\) The quantity and quality of the nanotubes obtained by this method depend mainly on the metal/carbon ratio, reaction environments and the pressure of the container used.

**Laser Growth** The laser growth method is commonly used for the generation of SWNTs. In laser growth, metal catalyst is added to a graphite source target, which
is then evaporated by a high power laser inside a furnace held at a high temperature, (around 1200 °C). SWNTs grow in the condensing vapour and an deposited on the colder parts as they are swept out of the furnace by an inert gas current. The laser power introduced in this method could be either pulsed laser or continuous laser. Since the pulsed laser can provide more intense energy, it is more used than the continuous laser. The laser growth method synthesised SWNTs exhibited higher yield than the SWNTs generated by arc discharge methods. However, the production rate was relatively low, and the pulsed laser vaporisation or laser ablation was infrastructure and energy intensive.

Chemical Vapour Deposition (CVD) In this method, a small transition metal catalyst, (nearly always Fe, Ni, Co metal nanoparticles) facilitate the decomposition of a hydrocarbon vapour and helps extrude a nanotube or nano-fibre at moderate temperatures (600 °C to 1200 °C) inside a furnace. The resulting nanotubes materials are then collected at room temperature. The carbon sources are typically could be acetylene (C₂H₂), ethylene (C₂H₄), ethanol (C₂H₅O) or methane (CH₄), blended with ammonia, nitrogen or hydrogen. To grow SWNT with a very small diameter by CVD method (nearly 1 nm), metal nanoparticles must be provided with controlled shape and sizes. Those metal nanoparticles may be prepared in advance, or produced simultaneously inside the furnace by the decomposition of a metal containing salt (such as nickel formate) or organic molecule (such as ferrocene). Since the metal nanoparticles are intrinsically unstable, special steps must be made to stabilise them or to use those metal particles as soon as they are formed. The generated nanotubes may grow on catalyst surfaces or in the vapour phase. The mechanism of the CVD method includes dissociation of hydrocarbon molecules catalysed by a transition metal, dissolution and deposition of carbon atoms on the substrate and precipitation from the saturated metal particles was known to induce the formation of the SWNTs tubular structure. It was found that this method typically produces SWNTs which are “impurified” with double- or mulit-walled SWNTs too.
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**Plasma-enhanced Chemical Vapour Deposition** The basic concept is similar to thermal CVD, except that the hydrocarbon feedstock is introduced by plasma, which provides energy for rapid decomposition and lower apparent growth temperatures.\(^{132}\) Table 1.4 highlights some advantages and disadvantages of different carbon nanotube growth methods which discussed above.

**Table 1.4 Advantages and disadvantages of different nanotube growth methods**

<table>
<thead>
<tr>
<th>Growth method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric Arc Growth</td>
<td>Very straight</td>
<td>Low purity</td>
</tr>
<tr>
<td></td>
<td>High crystallinity</td>
<td>Gram quantities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Moderately expensive</td>
</tr>
<tr>
<td>Laser Growth</td>
<td>High quality SWNTs</td>
<td>Low purity</td>
</tr>
<tr>
<td></td>
<td>Diameter control</td>
<td>Gram quantities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very expensive</td>
</tr>
<tr>
<td>Chemical Vapour Deposition</td>
<td>High purity</td>
<td>Low quality(defects)</td>
</tr>
<tr>
<td></td>
<td>Relatively cheap</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Structural flexibility (other forms)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diameter controlled via catalyst</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alignment / position control</td>
<td></td>
</tr>
<tr>
<td>Plasma-enhanced Chemical Vapour Deposition</td>
<td>Fast growth rate</td>
<td>Increased disorder</td>
</tr>
<tr>
<td></td>
<td>Excellent alignment / position</td>
<td>Etched tubes</td>
</tr>
<tr>
<td></td>
<td>Low growth ‘temperature’</td>
<td>Reduced yields</td>
</tr>
<tr>
<td></td>
<td>High purity</td>
<td></td>
</tr>
</tbody>
</table>

Regardless of which synthesis method is followed, all carbon nanotubes contain certain amount of impurities in their as-made state, such as amorphous carbon, fullerenes, metallic nanoparticles, multi-shelled carbon nanoparticles, nano-crystalline graphite, as well as various contaminations depending on the support substrate used,
like silicon substrate and copper. Depending on the synthesis route, some defects or surface disorders may also present onto the surface of carbon nanotubes. Those impurities may affect the properties of the tubes.

1.3.1.2 Purification of carbon nanotubes

As described in the previous section, there are always some impurities coexisting with generated carbon nanotubes. In addition to the catalyst, the impurities contain carbonaceous carbon and metal catalyst particles, and the amount of the impurities present commonly increases with the decrease of the CNT diameter. Carbonaceous impurities normally contain amorphous carbon, fullerenes, and carbon nanoparticles or polyhedral carbons, which are introduced as the non-fully reacted carbon source or reaction by-products. Metal impurities are commonly present due to the residues from the transition metal catalysts, especially in CVD preparation method. Among the carbonaceous impurities, fullerenes can be relative easily removed due to their solubility in organic solvents such as toluene, and amorphous carbon can be removed by oxidising the as-made CNTs material under gentle conditions, due to the surface defects and non-crystalline structure. These can then washed out using a combination of organic solvents. Polyhedral carbons are harder to oxide or purify due to their similar oxidation rate to carbon nanotubes. In some cases, the carbon and metal nanoparticle impurities sometimes were found to combine together to form a metal encapsulated carbon shell structure, which makes them not reactable as they cannot be dissolve even in acids.

The purification of carbon nanotubes normally involves three strategies: (1) chemical oxidation, (2) physical separation and (3) a combination of (1) and (2). The principle of the chemical purification strategy is to oxidise the carbonaceous carbon impurities and then solubilisation of the metallic impurities by acid treatment. In general, the chemical oxidation relies on gas phase oxidation, liquid phase oxidation and electrochemical-based oxidation technique. For the gas phase oxidation, the
carbon nanotubes are gradually purified by heating to 225 °C to 760 °C under an oxidising atmosphere. The gas phase commonly used are air\textsuperscript{135,136,137}, a mixture of Ar, O\textsubscript{2} and water\textsuperscript{138}, a mixture of Cl\textsubscript{2}, H\textsubscript{2}O and HCl\textsuperscript{137} as oxidant reagents. Gas phase oxidation is a simple method for removing carbonaceous impurities without strongly introducing sidewall defects, but it cannot directly remove metal catalysts and some large graphite particles. Liquid phase oxidation can simultaneously remove both amorphous carbon and metal catalyst. The commonly used oxidants for liquid phase oxidation include HNO\textsubscript{3}\textsuperscript{139,140}, H\textsubscript{2}O\textsubscript{2} or a mixture of H\textsubscript{2}O\textsubscript{2} and HCl\textsuperscript{141}, a mixture of H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}, KMnO\textsubscript{4} and NaOH\textsuperscript{142,143}, and KMnO\textsubscript{4}\textsuperscript{144}. There are drawbacks of the liquid phase oxidation method too, as this can introduce reaction products on the surface of CNTs, add functional groups, and destroy CNT structures, including the shortening and opening CNTs. Electrochemical oxidation method has been carried out to remove a small amount of surface defects: Fang and co-workers has reported these into the investigation of a electrochemical cyclic voltammetry (CV) oxidation behaviour of an arc discharge derived SCNTs sample in KOH solution\textsuperscript{134}.

The physical purification methods can remove the graphitic sheets, carbon nanospheres, aggregates without introduce surface defect damages to the aromatic structure. Physical-based methods typically include filtration\textsuperscript{145}, chromatography\textsuperscript{146}, centrifugation\textsuperscript{147}, electrophoresis\textsuperscript{148}, and often involve high temperature processes, commonly involve annealing 1000 °C to 2800 °C.\textsuperscript{149,150,151} All these purification methods have been extensively investigated in the search to investigate pure nanotubes natural properties, such diameter size and tubes gravities.

The combination of chemical purification and physical purification is carried out by a member of different multi-step reactions and several different groups have published a range of reports\textsuperscript{152,153}. Owing to the diverse nature of the production methods, the combination purification strategies always applied to remove target impurities. This method can lead to high yield and high-quality CNT products but
required careful design, and fully studies are needed for the optimum purity to be reached.

1.3.1.3 Functionalisation of carbon nanotubes

Functionalisation of carbon nanotubes has already become a very important research field. As some functional groups are grafted on the surface or trapped within the inner space of carbon nanotubes, those functional groups can alter the properties of carbon nanotubes, such as increasing the SWNTs solubility, exfoliate and mono-disperse bundles of tube, include higher order structures using self-assembly and so on. Although the functionalisation of SWNTs has attracted some significant attention, the chemistry of functionalised carbon nanotubes is very challenging due to the poor solubility and low reactivity of the SWNTs. The functionalised results could be very hard to characterise due to batch-to-batch recording in SWNTs starting materials available.
Figure 1.14: Functionalisation possibilities for SWNTs: (A) defect-group functionalisation; (B) covalent sidewall functionalization; (C) non-covalent stacking functionalisation with surfactants; (D) non-covalent stacking functionalisation with polymers and (E) endohedral functionalisation with nanoparticles\(^\text{154}\)

The strategies of functionalisation of carbon nanotubes could be divided into five types: (1) surface defect-group functionalisation, (2) covalent sidewall functionalisation, (3) non-covalent stacking functionalisation with surfactants, (4) non-covalent stacking functionalisation with polymers and (5) endohedral functionalisation with nanoparticles. The Figure 1.14 gives a schematic representation of these functionalisation strategies. The covalent functionalised strategies include surface defect-groups functionalisation and covalent sidewall functionalisation. The oxygen-containing surface defects can be introduced onto the surface of SWNTs by oxidation reactions.\(^\text{144}\) It has been reported that the use of highly reactive reagents to directly attack the side wall is another way to functionalise carbon nanotubes.\(^\text{155}\) The use reactive agents and methods, borrowed and adapted from \(\text{C}_{60}\) chemistry, such as the Bingel\(^\text{156}\) reaction and radical trapping reaction\(^\text{157}\) have been particularly
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successful.

It has been found that the non-covalent functionalisation strategies for carbon nanotubes can avoid the introducing of defects into the carbon nanotubes structure. The non-covalently functionalisation methods are based on surface association and van der Waals Interactions.\textsuperscript{158} For example, a lot of effort has been devoted to study the interaction between long chains of DNA and nanotubes.\textsuperscript{159,160} It is believed that the nanotubes are in the hydrophobic interiors of the corresponding micelles, which results in stable dispersions. When the hydrophobic part of the amphiphile contains an aromatic group, an especially strong interaction results, because of an effective and cooperative, extended $\pi$-$\pi$ stacking interactions which can then be form with the graphitic sidewalls of the SWNTs. This effect was demonstrated in the aggregation of CNTs with N-succinimidyl-1-pyrenebutanoate.\textsuperscript{161}

For the endohedral functionalisation strategy, C$_{60}$ molecules have also been found to be encapsulated into the inner space of nanotube to form a hybrid C$_{60}$@SWNTs structure.\textsuperscript{162,163} Filling nanotubes with metal nanoparticles have been also successful in both original growth method\textsuperscript{164} and liquid phase filling methods\textsuperscript{165,166}. Recent research reporting the encapsulation of metallofullerene has also been published.\textsuperscript{167,168,169,170} It is also reported that graphene nanoribbons are easier self-assembly together inside the inner space of carbon nanotubes.\textsuperscript{171} Since carbon nanotubes are highly heterogeneous, many functionalisation techniques have been used in an attempt to separate single-wall nanotubes samples, which include dielectrophesis, selective functionalisation, wrapping with DNA and density gradient centrifugation.\textsuperscript{172} All those methods are limited to small volume and low yield, but once the single wall carbon nanotubes are separated, the unique diameter and chirality of SWNTs could be studied, and it was shown that, depending on diameters and lengths, such SWNTs can be highly coloured.\textsuperscript{159}
1.3.1.4 Carbon nanotubes as synthetic scaffolds for photovoltaics

Carbon nanotubes have a variety of attractive features which make them a suitable material for electrochemistry: high electrical conductivity, natural hydrophobic and adjustable porosity. One application for which these have been widely studied results to the use of carbon nanotubes in electrochemistry, and the application of carbon nanotubes as substrates considered for the improvement of traditional solar cells electrode designs. In addition, the carbon nanotube can absorb light in both UV and near-IR range. It has been investigated that the use of SWNTs can add benefits both in terms of performance and durability of PVs.\textsuperscript{173,174}

For organic bulk heterojunction solar cells, the diffusion range of excitons remained a problem since the diffusion can only occur in a couple of nanometres near the interface between donors and acceptors. In this case, one of the improvements of OSCs is the introducing of mixed donor and acceptor species and provides the device with a much larger contact interface between donors and acceptors. The diffusion range of excitons in an organic photovoltaic device is approximately in the order of 10 nm. When mixing the donors materials and carbon based nanomaterials acceptor materials together, the actual size of the donor layer as well as that of the acceptor are smaller than the diffusion range and the domain can be reduced to several nanometres. Thus, the excitons can diffuse to the interface much easier and quicker. SWNTs can potentially be applied as the acceptor material in this improvement, due to their unique properties, like low electricity resistance and large surface area. Until recently, followed by this principle, some studies reported SWNTs have been introduced in OSCs as the acceptor materials,\textsuperscript{175} Luyao Lu and co-workers have demonstrated a method to use N-doped multiwall carbon nanotubes as acceptor materials which led to the achievement of highly efficient polymer bulk heterojunction solar cells.\textsuperscript{176} It has also been found that in dye sensitised solar cells, the electron injection from the excited state of dye molecule occurs on timescales much faster than the excited state decay and recombination of the injected electron with the dye cation\textsuperscript{177,178}. Thus,
similar to BHJ, it has been found that when single wall nanotubes were used as the material of choice for providing solar cells with necessary electrochemical properties, the resulting solar cells have been significantly improved in terms of efficiency.\textsuperscript{179,180,181} Therefore it is always demonstrated that SWNTs can play an important role in improving the charge separation, and it was shown that the injected electrons for conduction become faster in the presence of the SWNT scaffold.\textsuperscript{182} Some recent research also showed that when a quantum dot-single wall carbon nanotube complex, the resulting solar cell shows a good performance of light covert efficacy.\textsuperscript{183}

1.3.2 Graphene oxide and graphene

1.3.2.1 Introduction of graphene oxide and graphene as materials of choice for PVs

Graphene rapidly became one of the most popular research area since it was discovered by A. K. Geim and K. S. Novoselov at the University of Manchester, by using a deceptively simple Scotch tape method.\textsuperscript{116} The reason behind this rapidly development of this material is due its promising properties: graphene has a significant large surface area, \(2630 \text{ m}^2 \text{ g}^{-1}\), which is nearly hundreds times larger than normal carbon material; it have high intrinsic mobility, \(200000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\);\textsuperscript{184,185} graphene also obtain high Young’s modulus, which around 1.0 TPa;\textsuperscript{186} the thermal conductivity of graphene is \(5000 \text{ Wm}^{-1}\text{K}^{-1}\) and its optical transmittance is up to 97.7\%\textsuperscript{187}. Beside these physical characteristics, graphene sheets have special electronic structure, giving this material remarkable electronic properties, for instant the anomalous quantum Hall effect\textsuperscript{188} and its amazingly high carrier mobility at a relatively high charge carrier concentration and at room temperature.\textsuperscript{184} All these properties rendered graphene as a new material considered to be in next-generation applications of several different types of nano-electronic devices of relevance to sensing and biosensing, transparent conductive films construction, fuel cells, electrical energy storage and also structural materials design.
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The lattice of a monolayer of graphene sheet lattice consists of two equivalent sub-lattices of carbon atoms bonded together with σ bonds. The delocalised network of electrons within a graphene sheet is due to each carbon atom in the graphene lattice obtaining a π orbital.

There are normally three strategies to produce graphene: (1) exfoliation of graphite in solvents, (2) micromechanical exfoliation and (3) epitaxial graphene. The production of graphene by micromechanical exfoliation was introduced by Ruoff and co-workers.\(^{189}\) Although the micromechanical exfoliated graphene has a high quality and leads to the rapid development of graphene characterisation, this method are not suitable to larger material production scales and thus cannot meet the requirements for most commercial applications. The direct production of graphene by exfoliating graphite in common organic solvents, such as DMF and NMP, was introduced, and this included a prolonged time under the ultrasound treatment.\(^{190}\) This direct conversion can produce graphene with low a defect ration, but besides the fact that it is time and energy consuming, it is still limited by the large size and thickness of the sheets produced.\(^{191}\) It is also reported that a high-quality thin graphene films could be produced from fast electrochemical exfoliation.\(^{192}\) The epitaxial graphene is introduced by chemical vapour deposition (CVD) on metallic catalysts. This method has been shown to be used in the generation of a high quality monolayer or several layers graphene with very thin dimensions and which is highly conductive.\(^{193,194,195}\) The epitaxial graphene production is currently the most widely studied method. The large scale production of graphene of high carbon purity by CVD approaches could provide the desired material in sufficient quantity for a host of likely applications, as well as for fundamental science. But, the challenge for epitaxial graphene production is the efficient transfer of the generated graphene sheets from the metal substrate to other substrates. Until recently, a new method for graphene generation is emerging, which is described as substrate-free gas-phase synthesis of graphene.\(^{196}\) This method
provides a new approach to the synthesis of graphene.

![Schematic representation of graphene oxide sheet and relevant oxygen site defects.](image)

**Figure 1.15:** Schematic representation of graphene oxide sheet and relevant oxygen site defects. (Model adapted from a literature\(^{197}\))

As discussed above, although graphene has several different promising properties, the large generation is still very challenging. In order to find a cost-effective method for the production of graphene, graphene oxide re-emerged as an intense research area.\(^{197}\) The graphene oxide has similar structure properties compared with graphene. Graphene oxide can be regarded as a defective graphene sheet, which functionalised by introducing oxygen containing groups (including carboxyl groups, hydroxyl groups and carbonyl groups) onto its surface. The properties of graphene oxide change with the changing of the percentage of oxygen groups. Figure 1.15 is the schematic representation of graphene oxide sheet.

The generation of graphene oxide is via the direct exfoliation of graphite oxide. Graphite oxide has a similar structure to graphite, but the plane of carbon atoms in graphite oxide is heavily decorated with oxygen containing groups, which not only enlarge the distance between each layer, but also make the thin layer hydrophilic and thus they are increasing soluble in aqueous phase. Thus, graphene oxide can be exfoliated form graphite oxide by moderate sonication. Generally, graphite oxide is synthesised by either Brodie,\(^{198}\) Staudenmaier\(^{199}\) or Hummers method\(^{200}\). Brodie and Staudenmaier used a combination of potassium chlorate (KClO\(_3\)) with nitric acid (HNO\(_3\)) to oxidize graphite, while the Hummers method involves the treatment of
graphite with potassium permanganate (KMnO$_4$) and sulfuric acid (H$_2$SO$_4$). The level of the oxidation can be varied on the basis of the method, the reaction conditions and the precursor graphite used.

After the introducing of oxygen containing groups onto the surface of a graphene sheet, graphene oxide sheets are significantly hydrophilic and the water molecules can intercalate into the inner layer space. Thus, the graphene oxide can form a stable aqueous colloidal suspension. The inner distance between each graphene oxide sheet in a water colloidal suspension could vary from 6 to 12 Å, depending on the increasing humidity and oxidation and this can make it characterisation particularly challenging. Recent studies showed that the water dispersed graphene oxide exhibits a negative surface charge. The negative charge on graphene oxide surface leads to electrostatic repulsion between negatively charged graphene oxide sheets and contribute to making of very stable the aqueous suspensions. The negatively charged surface of graphene oxide in water dispersions is a very important property when applied to the role graphene oxide in substrate deposition processes from dispersed phases as the surface charge of the substrate material should be matched.

1.3.2.2 Reduced graphene oxide (rGO)

The reduction of graphene oxide was applied as one of the alternative ways to produce graphene in bulk generation. The reduction of graphene oxide can be carried out by several methods. Graphene oxide can be reduced by a high temperature annealing process. The thermal reduced process can decompose the oxygen containing groups and exfoliate graphene oxide sheet at the same time. According to Gao’s research, the critical dissociation temperature (Tc) of hydroxyl groups attached to the edges of GO is 650 °C and only above this temperature hydroxyl groups can be fully removed. After the thermal annealing at temperatures of 700 °C to 1200 °C in vacuum, the hydroxyl groups can be fully eliminated. The good reduction effect by
thermal annealing at around 1000 °C was also proved by the high conductivity reported by Becerril\textsuperscript{204} and Wang\textsuperscript{205}. As theory predicted, the common annealing reduction has to be carried out at 900 °C to 1100 °C, such that the oxygen groups on the surface of graphene oxide can be efficiently removed and the ratio of C/O may be significantly increased.\textsuperscript{206} As an alternative process, microwave irradiation reduction of graphene oxide has been carried out.\textsuperscript{207,208} The main advantage of microwave irradiation over other heating source is that the heating of substances can be uniform and rapid. By treating graphite oxide powders in a commercial microwave oven, graphene oxide can be readily reduced to product within 1 min.

Another type of graphene reduction is carried out by introducing chemical reducing agents. The chemical reduced graphene oxide can be obtained by processes carried out at room temperature or moderate heating atmosphere. The most common and widely used reducing reagent is hydrazine or hydrogen hydrate.\textsuperscript{209,210,211} The reduction by hydrazine and its derivatives, such as dimethylhydrazine\textsuperscript{212}, can be addressed by adding the liquid reagents to a GO aqueous dispersion. This results in the formation of agglomerated graphene-based nanosheets due to the increase of synthetic’s hydrophobicity. The use of NaBH\textsubscript{4} for this process was also reported recently. This can be used as the reducing reagent to produce rGO.\textsuperscript{213} As discussed above, the use of thermally reducing and chemically reducing reagents are the most common methods applied in the reducing progress of graphene oxide. A novel method combines thermal and chemical reducing methods together emerged recently: hydrothermal process where overheated supercritical water can play the role of a reducing agent.\textsuperscript{214,215}

Other methods, like photo-reduction\textsuperscript{216}, photocatalyst reduction\textsuperscript{217} and electrochemical reduction\textsuperscript{218} have all been reported for rGO production, used to reduce graphene oxide, compared with the thermal reduction and chemical reagent reduction methods, these methods are not suitable in bulk reduction of graphene, as
the reducing rates are not very applicable for large scale applications.

1.3.2.3 Graphene and graphene oxide as material scaffolds in photovoltaic devices

Since the graphene sheets hold promising thermally conductive, electronic and mechanical properties, graphene and its divertive/graphene oxide, are considered as scaffolds towards the construction of next-generation flexible photovoltaic devices. It was reported by Xuan Wang and co-workers that by employing graphene as a material for the electrode of dye sensitised solar cells. As made obtained graphene films exhibit a high conductivity of 550 S/cm and a transparency of more than 70% over 1000–3000 nm. Gurpreet Singh Selopal reported that by employing graphene as a transparent front contact layer material, a value of photo conversion efficiency as high as 2% has been recorded for the best cell, under one sun irradiation.

Similarly with the care of SWNTs, the graphene and graphene oxide can also be used as electron acceptors due to their low reduction potential. For graphene sheets, the electrons can freely move at room temperature. This significant electron transport ability renders graphene an ideal material to assist the charge separation and conduction in solar cells systems. Considering its size, a graphene sheet can measure up to the micrometre range, which is a thousand times larger than the common donor molecules used in DSSCs. As a result, graphene can provide abundant space for donor molecule to attach to either covalently or non-covalently.
Additionally to the considerations discussed above, Jacob Tse-Wei Wang also reported an electron collection layer consisting of Graphene-TiO$_2$ nanocomposites as components of thin film perovskite solar cells. This showed a remarkable photovoltaic performance with a power conversion efficiency up to 15.6%. Recently, Jian Zhi demonstrated that a graphene, TiO$_2$ and a dye molecule complex anode structure (as showing in Figure 1.16), can achieve a power conversion efficiency of 6.41%. This is 56% higher than the care when the pristine TiO$_2$ material was used for the anode. This design confirmed that graphene can be used as an acceptor material in organic solar cells. Other researchers found that CdS and graphene can lead to the high photo degradation rate under visible light irradiation and similar results have also been found for CdSe quantum dots with graphene oxide. As such, although graphene and graphene oxide are new materials, they are already becoming of interest for solar cells and related PVs devices consideration and study.
1.3.3 Characterisation methods for carbon nanomaterials

*Transmission electron microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM):*

TEM and HRTEM are the most direct and important method to obtain surface morphology information of carbon based nanomaterials. Their physical basis relies on the generating a beam of electrons, which is transmitted through an ultra-thin specimen and interacts with the specimen as it passes through. Due to the extremely small wavelength of electrons, 0.00025 nm (2MeV), TEM/HRTEM can generate a much more detailed image of an ultra-small objective than an optical microscope. The range of image scale is typically in between 1 nm and 1 µm. The resolution scale of TEM/HRTEM can be as low as even the sub-Å dimension. In TEM, the electron beam is generated by using a LaB₆ crystal as the source. The emitted electrons can be then accelerated by an electric potential. Electromagnetic lenses are applied to force the electron beam to hit the sample in a precise spot. Electron diffraction is a method of choice for measuring a sample’s atomic structure, but the depth of the sample could also affect the recorded image. For this reason, the sample preparation is particularly important, especially for carbon nanomaterials which are known to self-aggregate rapidly. Heavy elements, due to their high atomic number, scatter electron beams more than the light elements (C, H, N, B), which gives image contrast. In other case, the measured sample can be overlapped together and this could also generate image contrast. The contrast formed in HRTEM is a consequence of the difference in phase for the differently scattered electrons.

Although TEM/HRTEM are crucial methods for giving atomic structure information in nanomaterials, these methods can only examine small amounts of materials. During the measurement, electron beam damage may potentially introduce physical damages into the measured samples, depending on the sample’s properties. There are several different imaging modes which can be applied in the measurement,
including mapping chemical composition within 1 nm resolution. High-resolution transmission electron microscopy (HRTEM) is an imaging mode of TEM that allows the imaging of the crystallographic structure of a sample on the atomic scale. Recently, Jannick Meyer and co-workers described the direct visualization of light atoms, such as carbon and even hydrogen, using TEM and a clean single-layer of graphene substrate.\textsuperscript{224}

In this project, the TEM and HRTEM will be used to specifically obtain information of all carbon nanomaterials and their complexes before and after functionalised with small molecules. Specifically the presence of the heavier atoms along the walls of the tube before/after functionalisation, and a comparison before/after samples helps identify whether defects are introduced and any heavy atoms are attached to the surface of carbon nanomaterials.

\textit{Scanning Electron Microscopy (SEM):}

The large scale surface information of the carbon nanomaterials and nanohybrids of interest can be obtained by this method. SEM can produce a very high-resolution image of a sample surface, revealing morphology on a scale about less than 1nm to 5 nm in size, by scanning it with a focused beam of electrons. The energy of the scanning electron ranges from 0.2 keV to 40 keV. These energy-rich electrons interact with the sample during the measurement and cause the emission of low energy, secondary electrons and backscatter of incident electrons. The secondary electrons are reflected from 10 to 100 nm depth in the sample, which can in turn be used to determine the morphology of the sample. Backscattered electrons come from 1 – 2 \( \mu \text{m} \) and provide information about atomic number found in the sample. The backscatter intensity depends on the average Z value of the atom situated within the interaction volume. SEM can also be used to address the assessments of size and aspect ratio. With this specific technique, SEM can provide 3D images which can help
provide structural information. By using SEM images, one may be able to distinguish single-walled nanotube bundles, multi-walled carbon nanotubes, carbon fibre and other nanorods or determine the crystallinity of the structure.

In this project, the SEM images have been applied to obtain surface morphology information for the complex nanomaterials synthesised and compare these to the surface of the starting materials (carbon nanomaterials) before and after its functionalisation and/or purification.

**Energy Dispersive X-ray Spectroscopy (EDX):**

Energy dispersive X-ray spectroscopy is a common technique, frequently formed in practice as coupled with TEM and SEM, applied in the study of the elemental analysis (for chemical characterisation). The physical basis relies on the fact that each element has a unique atomic structure which allowing unique set of peaks on its X-ray emission spectrum. Since the X-ray radiation in EDX exits the sample and hits the detector, within the microscope used, EDX analysing may be used to verify the elemental composition of the materials present in carbon nanomaterials in addition to TEM and SEM imaging, and within the field of view of the same samples. In this project, EDS is applied to analyse the presence of specific element to demonstrate their incorporation within a hybrid/composite nano-structure.

**Atomic Force Microscopy (AFM):**

AFM is a very sensitive and high-resolution type of scanning probe microscopy. In AFM, a force-sensing or imposing microscope provided with a nano-dimensional (≤10 nm size) scanning tip, probes the surface of a material deposited onto a support by sensing a force between the surface of the material and the tip. The interactions can generate a potential called binding energy $E_b$. The information is then collected via monitoring the force change between sample surface
and probe tip. The quality of the AFM images obtained is mainly dependent on the quality of the measuring tips used. AFM tips are usually made of silicon nitride, silicon oxide, silicon or similar hard materials and they can often show physical-chemical interacting with the substrate that are being analysed. Recently, AFM tips made from SWNTs have led to the development of chemical force microscopy. The most common methods applied in AFM are Contact Mode (CM) and Tapping Mode (TM). Surface profiles can be obtained in the contact mode by the scanning of a cantilevered AFM tip across a substrate surface. Tapping mode AFM (TMAFM) is carried out in a similar way with the CMAFM, but in this case the tip is oscillated near resonance with ca 50 to 500 kHz. AFM is commonly used to characterise nanoscale structures, to study the surface condition, precise diameter and length. AFM can be used to apply forces for the quantification of nanotube mechanical strength or for the measurement of carbon nanomaterials electromechanical properties. By measuring the whole area of a deposited substrate, the AFM images can also reflect the level at with the carbon nanomaterials are being dispersed onto the support. In this project, the TMAFM was used to distinguish the differences between different linking strategy functionalised carbon materials, and to study the size/shape of nanomaterials.

Raman Spectroscopy:

Raman is a spectroscopic technique which is extensively used to study vibration of SWNTs and graphene oxide/graphene samples. It provides a quick means of determining the degree in crystallinity of graphitic carbon based materials and the presents the size of single-walled nanotubes. The physical basis of Raman spectroscopy is that a beam of monochromatic laser light is applied in a pulsed manner though the sample. The photons of this laser beam interact with the sample and then scatter out. The scattering of these photons can be either elastic or inelastic. In fact, most of the photons are reemitted in an elastic manner, which means that the
frequency of the photons remains the same. Inelastic scattering means that all those photons which are reemitted with a different frequency by releasing energy via the Stokes scattering, or by removing energy via anti-Stokes scattering, are collected by spectrometer and used for Raman spectroscopy. The Raman spectroscopy may be used for the characterisation or dispersion of SWNTs in common solvents, but normally such materials are characterised by its solid state Raman spectroscopy. This is an essentially the main, reliable and affordable method for the characterisation of carbon nanomaterials in bulk and particularly of relevance for industrials scale applications.

There are generally four peaks which can be observed by Raman spectroscopy: (a) the G band (~1580 cm\(^{-1}\)) which is due to the primary graphitic mode, related to the in–plane tangential vibrations of the nanomaterials; (b) the D band (~1300 cm\(^{-1}\)), a defect band which corresponds to the sp\(^3\)-hybridised carbon present in the sample as SWNTs defects and impurities; (c) the G’ band (~2600 cm\(^{-1}\)), commonly called 2D band associated with graphiticity; and (d) the Radial breathing mode (RBM), which is due to the radial expansion and contraction of a nanotube and which can be applied to calculate the average diameter of the carbon nanotube stands present in the sample. The D/G band intensity ratio is always considered as a measure of the purity and quality of the carbon materials samples investigated. SWNTs spectra tend to obtained from tubes where the laser energy matches the band gap. In this project, Raman spectroscopy was used to investigate the inner structure of the carbon nanotubes, graphene oxide and reduced graphene oxide before and after chemical functionalisation with small materials.

1.4 Summary to Chapter 1 and Aims of This Project

As introduced in this Chapter, and due to the social requirements include by the diminishing of the fossil fuel usage and even increasing demands for energy, the topic of solar energy is prominent in both academic research and government policy.
In solar energy industry, solar cells techniques currently play a dominate role. The current (commercially available) first generation solar cells present good power conversion efficiency but due to the high cost and not very eco-friendly availability of materials and their production progress, the next generation solar cell design is utterly needed.

Compared to other new generation solar cells and despite recent progress made by solid state image with perovskite, organic solar cells exhibit further promise. It has been demonstrated that in organic solar cells, especially in organic bulk heterojunction (BHJ) and dye sensitised solar cells (DSSCs), small molecules can be applied as the light harvesting absorber. For both BHJ solar cells and DSSCs, despite differences in structure the basic operating principle remain the same: the light absorber works as “donor”, harvesting light, generating exited electrons and injecting them into the “acceptor”, and then the acceptor materials transferring the charge to external current.

Nowadays, in both BHJ and DSSCs research areas, almost all attempted efforts are based on introducing new donor/accepter materials and improving the electron diffusion efficiency within the system to increase the cell efficiency. This direction is crucial, and with the enhanced availability of carbon nanomaterials, it opens up new vistas in PVs design. Porphyrins are well demonstrated light harvesting dye molecules and can be used as “donor” materials in organic solar cells (OSCs).

It has also been demonstrated that the fullerene and porphyrin complexes investigated so far showed great promise as new synthetic scaffolds for new functional materials for photovoltaic applications, but only very few investigations into the device fabrication based on porphyrin oligomers and carbon nanotubes or graphene/graphene oxide have been carried out so far.
SWNTs and graphene/graphene oxides are exciting novel materials belonging to carbon nanomaterials class and having promising electronic and mechanical properties which make them even more interesting (when compared with fullerenes) from the perspective of their ability from hybrid combination with porphyrin molecule which can act as donor/acceptor systems in organic solar cells.

Thus, in this project, the aim was to carry out new studies towards the synthesis of nano-assemblies porphyrins and carbon nanomaterials. These already showed some great promises as new synthetic scaffolds for functional materials for photovoltaic applications but have not yet been investigated in full. The porphyrin molecules investigated here are those modified in both meso- and β-position and metaled to obtain a more tunable UV-vis absorption. Such functional porphyrins have been deemed challenging to synthesis on a lab scale. Generate new porphyrin complexes based on SWNTs and graphene/graphene oxides available via both supramolecular self-assembly (relying on the π-system of the carbon nanomaterials, will remain unaltered) and a more synthetically demanding (and disruptive) covalent approach linking methods. The efficiency of the two assembly methods will be compared.

The main project aims are:

1. To investigate the surface modification and functionalisation of SWNTs, synthesis of graphene oxide and reduction of graphene oxide. To perform characterisation by TEM, SEM, AFM methods and Raman spectroscopy.

2. To design and synthesis new highly conjugated and water soluble porphyrins with tuneable UV-vis absorption via incorporating with metal. To carry out characterisation by UV-vis, fluorescence spectroscopy and single photo confocal microscopy and investigate the molecular orbital energy levels of the porphyrin system in gas phase by DFT calculations.
3. To coat the carbon nanotubes with the most promising of the porphyrin systems synthesised, emerging from objective 2, using a covalent as well as a non-covalent binding technique. To characterise the resulting materials by TEM, SEM, AFM microscopy, Raman and fluorescence spectroscopy and evaluate the nature of the electronic interactions between the porphyrin and the nanotube scaffold.

4. To anchor the most promising porphyrin system emerging onto graphene oxide and reduced graphene oxide. To characterise the resulting nanohybrids by TEM, SEM, AFM microscopy, Raman and fluorescence spectroscopy and study the electronic interactions with the nanotube scaffold. Then, this work will give the possibilities in exploiting porphyrin and carbon nanomaterials complex into real photovoltaic applications.

5. To initiate future collaboration in solar cells device for build-up, testing the performance of new synthesised porphyrin complexes.

1.5 References to Chapter 1

Chapter 1 Introduction

Chapter 1 Introduction


8510-8514.


Chapter 1 Introduction


830-833.


Chapter 2 Synthesis of Graphene Oxide, Reduced Graphene Oxide and Modifications of Single-Walled Carbon Nanotubes

2.1. Overview

Chapter Two describes the synthetic methodologies and purification protocols in the preparation of graphene oxide (GO), reduced graphene oxide (rGO) and single-walled nanotubes (SWNTs). These methodologies adapted and improved previous protocols and are potentially suitable for scaling up. SWNTs Surface oxidation, which regarded as the basic purification method, is represented in the first instance. The main characterisation methods of purified SWNTs are TEM and Raman. Due to the harsh reaction conditions, the purification by surface oxidisation has introduced some defects and the impurities are not always efficiently removed. As a result, modified purification methods are described in this Chapter which consisted of microwave surface activation followed by acid wash and steam annealing purification. Furthermore, a Bingel reaction was carried out to functionalise the surface of SWNTs. This provided further linking sites, but also eliminates the influence of other surface defects.

Graphite oxide was used as a starting materials for GO and rGO. The synthesis of graphene oxide was performed by exfoliating graphene oxide sheets from graphite oxide. The graphene oxide can be further reduced yielding rGO. In this chapter, two reducing methods are described: first, the chemically and microwave reduced method and, second, the thermally reduced method.

The main characterisation methods of the resulting graphene oxide and reduced graphene oxide were undertaken though TEM, HRTEM and Raman
spectroscopy. In addition, the occurrence of a self-assembled hydrothermal graphene oxide hydrogel obtained by an adapted method is also discussed in this chapter. Graphene oxide hydrogel generated via hydrothermal heating exhibits a microporous 3-dimensional structure, which can be potentially used as synthetic scaffold for composite materials.

2.2. Results and discussions

2.2.1. Surface oxidation of SWNTs

![Figure 2.1: Schematic representation of surface oxidation of SWNTs.](image)

Surface oxidation of carbon nanotubes has been widely investigated in the past decades to improve the solubility of nanotubes in common organic and aqueous media. The carboxylate group introduced within the oxidation process can be converted to other covalently linked surface functional groups.\(^1\) In a typical experiment, the oxidation process has been carried out by using gas phase, electrochemical and liquid phase oxidations. The gas phase oxidation reaction has been performed by oxidising carbon nanotubes in oxygen atmosphere under 225 °C to 760 °C. The electrochemical cyclic voltammetry (CV) oxidation behaviour of SWNTs in KOH solution has also been reported.\(^2\) In this project, the oxidation of SWNTs was carried out in the liquid phase following an adaptation from the published methods, and samples of SWNTs
were treated with strong acid media containing 3 : 1 concentrated sulphuric acid : nitric acid mixture.

The SWNTs samples used in this oxidation process were Elicarb pre-purified (> 95 %) SWNTs provided by the Thomas Swan Company. After acid-assisted oxidation treatment, it can be found that some of the amorphous carbons still present in the original sample was removed. However, the strong acid used also introduced a lot of surface defects and damage the sp² carbon structure. Raman spectroscopy was carried out in order to check the presence of such defects in the sample.

2.2.1.1. Raman spectroscopy characterisation

![Raman spectra of intact SWNTs and surface oxidised SWNTs](image)

**Figure 2.2:** Raman spectra of intact SWNTs and surface oxidised SWNTs.

The Raman spectroscopy measurements were carried out to identify the inner structure of the Elicarb SWNTs (Thomas Swan) and the acid oxidised SWNTs. Figure 2.2 shows Raman spectrum of intact Elicarb SWTNs (black line) and surface oxidised SWNTs (red line). The starting material, Elicarb SWNTs, presents a D band at 1288
cm$^{-1}$ and a G band at 1584 cm$^{-1}$. The $I_D/I_G$ ratio of this starting material sample of SWNTs was found to be 0.11. Such a low $I_D/I_G$ ratio indicates a low level of surface defects and disorders. The sharp D band and G band also confirmed the provided tubes are single-walled rather than multi-walled in structure. The starting material SWNTs also exhibited two sharp peaks below 300 cm$^{-1}$ (one at 146 cm$^{-1}$ and the other one at 234 cm$^{-1}$), which correspond to the Radial Breathing Mode (RBM). These two latter peaks were found at 152 cm$^{-1}$ and 234 cm$^{-1}$. The Raman spectrum of intact SWNTs also exhibited several peaks from 300 cm$^{-1}$ to 1300 cm$^{-1}$, which were contributed by the residual metal nanoparticle catalyst impurities (majorly Fe residual). They were likely wrapped in carbonaceous material.

The acid-assisted oxidised SWNTs presented a D band at 1299 cm$^{-1}$ and a G band at 1589 cm$^{-1}$. The main D band and G band of oxidised SWNTs became broad compared with those found in the intact SWNTs. The $I_D/I_G$ ratio of acid oxidised SWNTs dramatically increased to 0.38. All those changes indicated that the acid-based chemical process introduced surface defects and damage the extended $sp^2$ carbon network of SWNTs. From the measured result, only one peak was observed in the RBM region of the spectrum, while the peaks from 300 cm$^{-1}$ to 1300 cm$^{-1}$ disappeared. The disappearance of the characteristic metal nanoparticle peaks and the occurrence of a single RBM peak indicated that the acid-assisted oxidation process can remove the impurities attached on the SWNTs surface. As a result, the acid oxidation process applied here has successfully introduced carboxylate groups onto the surface of SWNTs and effectively removed the impurities. However, due to the strong reaction conditions, the structure of SWNTs was extensively damaged.
2.2.1.2. Solid state investigations by TEM

Figure 2.3: TEM images of (a) intact SWNTs, scale bar = 100 nm; (b) acid oxidised SWNTs, scale bar = 50 nm.

TEM measurements were carried out to obtain the direct visualisation of acid oxidised SWNTs strands. Figure 2.3 presents the TEM images of intact SWNTs used as starting material and acid oxidised SWNTs. For the intact SWNTs images, those black dark points represent the residual nanoparticles within the sample. In the vicinity of the particles’ impurities, amorphous carbons were also observed. The length of the Swan SWNTs was in the order of micrometres. For the oxidised SWNTs it was found that the nanotubes were comparable to the single-walled structure and that the surface of SWNTs was damaged after treating with strong acid. Some of the tube ends also appeared opened. From the measurement, residual metal nanoparticle and amorphous carbon was also seen. The TEM measurement confirmed the acid oxidised reaction proceeded in agreement to previous studies reported in the literature³.
2.2.2. Microwave and acid wash purification of SWNTs

Figure 2.4: Schematic representation of the microwave treatment and acid wash purification of SWNTs.

In this project, the SWNTs were treated in the microwave followed by an acid washes. As discussed above, the starting SWNTs (provided by Thomas Swan Company) mainly contained three impurities: amorphous carbon, metal catalyst and multi-shell carbon nanoparticles. The microwave and hydrochloric acid wash purification process was used to remove those impurities step by step. It was reported that the acid reflux oxidise the metal nanoparticle and carbon impurity, which can then be removed by washing.\textsuperscript{3,4} However, the acid wash could only partly remove the metal nanoparticles attached onto the surface of SWNTs, and for those embedded metal nanoparticles, the acid wash purification process not provided promising results as showed in TEM images. In the purification process set in our laboratories, the microwave step was introduced to enhance the efficiency of the purification and the acid wash by heating the metal catalysts encapsulated in the carbonaceous from the interior. Figure 2.4 is a schematic representation of surface oxidation of SWNTs performed with the microwave step.

In the liquid phase oxidation, hydrochloric acid was used to remove metal...
nanoparticle. This is used as the hydrochloric acid can react with the metallic nanoparticles and convert these in soluble metal salt. After microwave reaction and washing with hydrochloric, the nitric acid was used as oxide agent to further react with metallic nanoparticle and oxidise the amorphous carbon. The nitric acid can break the sp² bonds and create defect sites within the hexagonal carbon framework. The carbonaceous materials emerging from the production process and attached onto the surface of SWNTs were irregular and defective in shape. In addition they have larger surface areas which may be exposed to oxidative reagents. Hence, amorphous carbon is particularly vulnerable to oxidation before the conversion of SWNTs, and then can be removed by filtration. As a result of the oxidative treatment, carboxyl or hydroxyl groups and surface defects were introduced on the SWNTs surface. To repair the defects introduced in the SWNTs, an annealing process was added at the end of this purification process.

The microwave and multi-acid wash purification process could successfully remove most impurities (as evidenced by Raman spectroscopy and TEM), but there were drawbacks. The purification via microwave and acid wash proved complicated and time consuming. Additionally, due to the strong oxidising and heating conditions, the yield of this purification was very low, only around 10%.
2.2.2.1. Raman spectroscopy characterisation

![Raman spectra of intact SWNTs and a comparison with the sample purified by a microwave and acid wash SWNTs.](image)

**Figure 2.5**: Raman spectra of intact SWNTs and a comparison with the sample purified by a microwave and acid wash SWNTs.

Raman spectroscopy was carried out to investigate the inner structure of the SWNTs purified by a microwave step followed by acid wash. As shown in Figure 2.5, the intact SWNTs presented a D band at 1288 cm\(^{-1}\) and a G band at 1589 cm\(^{-1}\), where the \(I_D/I_G\) ratio was 0.11. The microwave and acid wash purified SWNTs exhibited a D band at 1299 cm\(^{-1}\) and a G band at 1589 cm\(^{-1}\). After treatment with microwave and oxidation by acid, the \(I_D/I_G\) ratio of purified SWNTs increased to 0.40. The increased \(I_D/I_G\) ratio shown that nitric acid introduced defects and disorders onto the surface of SWNTs. Both intact SWNTs and the purified SWNTs showed clearly a band characteristic to 2D network at 2566 cm\(^{-1}\). The small peaks appeared between the RBM and D band in intact SWNTs also disappeared in the purified SWNTs sample, and this constituted the evidence that the metal nanoparticle impurities have been removed.
Figure 2.6: Raman RBM of intact SWNTs and microwave and acid wash SWNTs.

It can be seen from Figure 2.6 that the purified SWNTs exhibit two small peaks around 157 cm\(^{-1}\), while the intact SWNTs sample exhibited two peaks at 146 cm\(^{-1}\) and 234 cm\(^{-1}\). This RBM peak was then used to calculate the diameter of SWNTs by using the equation (1)

\[
\omega_{\text{RBM}} = \frac{234 \text{ cm}^{-1} \text{nm}}{D_{\text{SWNTs}}^5}
\]  

(1)

As a result, the intact SWNTs sample mainly consisted of strands with two diameters: one is 1.60 nm and the other is 1 nm, while the purified SWNTs consisted of strands with just one diameter of 1.50 nm. Since the RBM reflected the diameter information of the carbon nanotubes, the single peak in RBM indicated that the microwave and acid wash purification process successfully remove the impurities attached onto SWNTs surface.
2.2.2.2. Solid state instigations by TEM

Figure 2.7: TEM images of the purified SWNTs (using microwave treatment followed by an acid wash), (a) scale bar = 50 nm and (b) scale bar = 20 nm.

TEM characterisation was carried out to obtain the morphology information on the strands of SWNTs emerging microwave after the acid washing. Figure 2.7 showed the obtained microscopy results. From the TEM images (compared to the intact SWNTs TEM image shown at figure 2.3 (a)), it can be found that after the purification progress, the metal nanoparticles and the amorphous carbons had been almost entirely removed. The SWNTs strands exhibited relatively clear structures. As shown in images, the carbon nanotubes formed as tight bundles due to the strong van der Waals interaction. However, it could be also found that the surface of SWNTs strands purified by this method was partly damaged and some defects were observed on the surface. A higher resolution TEM imaging method would be more informative for charactering the solution of the purified SWNTs.
2.2.3. Steam annealing and purification of SWNTs

![Diagram of steam annealing process](image)

**Figure 2.8** Schematic representation of (a) steam purification of SWNTs; (b) reaction setup

As the purification methods described above (in section 2.2.1 and 2.2.3), surface oxidation and acid washing, were found to introduce new carboxyl defects or disorders onto the surface of the SWNTs and damage the extended sp² aromatic network at the same time. It was previously reported that steam, a mild oxidizing agent, can remove the amorphous carbon attached on SWNTs surface without introducing any defects but resulting yield remains extremely low. In this project, in order to eliminate the oxygen damage introduced by a steam-purification method, distilled water was used to generate steam. Distilled water was thoroughly degassed, while, before the annealing progress, the whole system was purged with argon. The steam was then introduced within the high temperature annealing process by bubbling argon.
through degased distilled water. The steam was then ready to be used. The steam can oxidise the amorphous carbon and “shave” those carbonaceous impurities down with flowing gas phase. Since the relatively mild oxide agent and the annealing process (which can repair the defects simultaneously) are used, this purification process can eliminate the damages introduced by the steam oxidation process. Followed by the steam purification process, metal nanoparticles were also removed by washing the material with hydrochloric acid.

The advantages of the steam purification process used here are that the amorphous carbon can be removed without introducing any further damage to the tubular structure. While, the drawbacks of the steam purification apparatus needed to be carefully controlled: each connection within the system should be tightly sealed to avoid air/moisture for linking into the system. A small amount of oxygen present within the system was found to dramatically decrease the purification yield. The yield of this purification process was relatively low, around 15% slightly higher than that reported in literature (where the air tight apparatus was not deemed crucial). Figure 2.8 is a schematic representation of steam annealing purification of SWNTs
2.2.3.1. Raman spectroscopy characterisation

![Raman Spectroscopy Image](image)

**Figure 2.9**: Raman spectra of intact SWNTs (red line) and steam purified SWNTs (black line).

Raman spectroscopy was carried out to study the inner structure of the steam purified SWNTs. As shown in Figure 2.9, the intact SWNTs (red line) presented a D band at 1288 cm\(^{-1}\) and a G band at 1589 cm\(^{-1}\), the \(I_D/I_G\) ratio was 0.11. The steam purified SWNTs revealed a D band at 1305 cm\(^{-1}\) and a G band at 1589 cm\(^{-1}\). The \(I_D/I_G\) ratio of purified SWNTs increased to 0.48. The increased \(I_D/I_G\) ratio shown that during steam purification process, the highly reactive steam affected the surface of the SWNTs and introduced some defects. It can also be found that both intact SWNTs and the purified SWNTs showed a clear band characteristic to the 2D network at 2560 cm\(^{-1}\). The small peaks which appeared between the RBM and D band in the intact SWNTs almost disappeared in the purified SWNTs. In this sample only one broad peak (around 500 cm\(^{-1}\)) remained, indicating that nearly all metallic nanoparticle impurities have been removed. Compared with the microwave and acid wash purification above described, the steam purified SWNTs didn’t need the initial treatment with microwave and nitric acid, which means that some metals could still remain trapped in amorphous carbon layers and not fully react with hydrochloric acid.
This could well be the reason for the nanoparticle impurities to remain in this sample.

![Figure 2.10: Raman RBM of intact SWNTs and steam purified SWNTs.](image)

It can be seen, from Figure 2.10, that the RBM of steam purified SWNTs exhibited a RBM peak at 157 cm\(^{-1}\) and the intact SWNTs exhibited two peaks at 146 cm\(^{-1}\) and 234 cm\(^{-1}\). As discussed before, the RBM peak can be used to calculate the diameter of SWNTs by using the equation (1), which suggested that the intact SWNTs sample contains mainly strands of two diameters: one is 1.60 nm and the other is 1.00 nm. The purified SWNTs contain mainly one diameter of 1.45 nm. The RBM of purified SWNTs indicated that the purification process does remove the impurities on the SWNTs surface. The relatively broader RBM peak found for steam purified SWNTs by Raman spectroscopy also indicated a low graphitic structure compared with that of the intact SWNTs used as starting materials.
2.2.3.2. Solid state investigation by TEM

![TEM images of microwave and acid wash SWNTs](image1)

**Figure 2.11:** TEM images of microwave and acid wash SWNTs, (a) scale bar = 50 nm and (b) scale bar = 50 nm.

TEM investigation was carried out to achieve the morphology information of steam purified SWNTs. Figure 2.8 showed the measurement results. From the TEM images, it can be found that metallic nanoparticles and amorphous carbon had been partly removed compared with the intact SWNTs TEM image shown at Figure 2.3 (a), which seem to be consistent to the Raman spectrum data. The purified SWNTs exhibited relatively clear structures and some of the tube ends had been opened after purification. The nanotubes were also bundled together, likely due to the strong van der Waals interaction.
2.2.4. Bingel reaction functionalised SWNT

2.2.4.1. Introduction of Bingel reaction functionalised SWNT

As described in previous chapter, Bingel reaction was well studied and investigated in fullerenes. Karl S. Coleman had demonstrated the Bingel reaction can be applied to SWNTs. The Bingel reaction of SWNTs was addressed here via [2+1] cycloaddition reaction. This functionalization reaction provided a generic method to modify the surface of SWNTs. This approach can potentially give access to covalently linking sites where no further defects are introduced. In this project, the reaction method was adapted from a method reported by Coleman et al. (see experimental section). The ethoxy groups introduced via Bingel reaction can be further modified to incorporate other functional groups and build new SWNTs complexes. Figure 2.12 is a schematic representation of a SWNTs functionalised under Bingel reaction.

**Figure 2.12:** Schematic representation of Bingel reaction functionalised SWNTs.
2.2.4.2. Spectroscopic characterisation by Raman spectroscopy

Raman spectroscopy was carried out to investigate the inner structure of the SWNTs functionalised by Bingel reaction. Raman data is shown in Figure 2.13. Intact SWNTs presents a D band at 1288 cm$^{-1}$, a G band at 1589 cm$^{-1}$ and a $I_D/I_G$ ratio of 0.11. SWNTs functionalised by Bingel reaction exhibited a D band at 1290 cm$^{-1}$ and a G band at 1588 cm$^{-1}$. The $I_D/I_G$ ratio of SWNTs functionalised by Bingel reaction (after Bingel-reaction treatment) was slightly increased to 0.16. An enhancement of the $I_D/I_G$ ratio can be assigned due to the surface functionalisation. The Bingel-reaction modified SWNTs also showed a 2D band at 2571 cm$^{-1}$.

Figure 2.13: Raman spectrum of intact SWNTs and Bingel reaction functionalised SWNTs.
Figure 2.14: Raman RBM of intact SWNTs (used as received form Thomas Swan) and Bingel reaction modified SWNTs.

The RBM of intact SWNTs and Bingel reaction modified SWNTs, shown in Figure 2.14, did not present a huge difference compared with previous surface modifications. The Bingel reaction did not introduce more defects onto the surface than the typical cycloaddition reactions\textsuperscript{8}. The Raman spectrum of Bingel reaction functionalised SWNTs remained largely unchanged with respect to the unreacted SWNTs, and exhibited two RMB peaks with maxima at 234 cm\textsuperscript{-1} and 145 cm\textsuperscript{-1}. This suggests that the formation of purified tubes with calculated diameters of mainly 1.02 nm and 1.64 nm and with rather narrow distribution ranges.
2.2.5. Synthesis of graphene oxide

Figure 2.15: Schematic representation of synthesis of graphene oxide (Alternative double bonds were removed for clarity, and to account for the defect sites).

High quality graphene oxide was synthesised by adapting a methodology reported in literature. This GO was used as the scaffold for further interaction with other small molecules. As a result, the synthesis of graphene oxide was one of the basic elements in this project. The graphene oxide was synthesised by the exfoliation method from oxidised graphite oxide. The graphite oxidised procedure was adapted from Hummer’s method in which potassium permanganate and manganese dioxide were introduced as the oxidising agent. Since the oxidation process introduces groups containing oxygen into the network of graphite oxide, the distance within each layer is enlarged during this process. The graphite oxide could then exfoliate in a liquid phase to afford graphene oxide.

The exfoliation of graphene oxide was carried out through an extensive sonication step. Since the long-time sonication may also introduce damage to the surface of graphene oxide, the progress of sonication was controlled within 15 minutes per section alternated by 5 minutes break. In the exfoliation process, different solvents could also be used to generate the final product. A 1 : 1 water and ethanol
solution was applied in this exfoliation process as graphene oxide is highly dispersible in this mixture. Un-exfoliated graphite oxide was separated from the mixture by centrifugation. The centrifugation speed and exposure time were tested and set as 3500 rpm for 30 minutes. It was found that part of the un-exfoliated materials can be separated when those conditions are used. The top 1/3 fraction of supernatant was collected and dried to afford the final graphene oxide product. The graphene oxide obtained was then characterised by TEM, Raman, UV-vis and FTIR spectroscopies to investigate its formation and its quality. Figure 2.15 is a schematic representation of the synthesis of graphene oxide.

2.2.5.1. Solid state investigation by TEM

![TEM images](image)

**Figure 2.16** (a) TEM images of graphene oxide, scale bar =200 nm, (b) SAED of graphene oxide, the scale bar =2 nm⁻¹, (c) HRTEM image of graphene oxide, scale
Chapter 2 Results and Discussions

bar = 10 nm and (d) HRTEM image of graphene oxide, scale bar = 10 nm.

The TEM measurement was carried out to obtain the surface morphology information of graphene oxide and in order to further investigate the lattice structure, selected area electron diffraction (SAED) and HRTEM was also introduced in characterisation. Figure 2.16 presented the measured results. It can be seen from Figure 2.16 (a) that graphene oxide exhibits sheet-like structures and that the size of these sheets can be up to micrometres in size. The image also indicated that there were some relatively small pieces of graphene oxide layered onto the bigger graphene oxide sheets. From the image, some “wrinkles” were also observed on graphene oxide sheets suggesting defective areas in the 2D network. More TEM images of graphene oxide are present in Appendix viii, Figure B.6.

Figure 2.16 (b) is the selected area electron diffraction (SAED), from the diffraction pattern, it can be seen there were 6 sharp and intense diffraction points which appeared in the first diffraction order indicating a crystalline structure. The distance from the 6 diffraction point to the centre is 4.1 Å, which correspond with the inter-planar spacing in graphene oxide. Apart from the 6 sharp diffraction points, several relatively light intensely spots were combined to afford a diffraction ring, this means that the graphene oxide was not a single layer structure, rather that, the graphene oxide obtained constitutes of a few layer sheets overlaid. Those sheets are rotationally oriented with respect to each other and the properties of each of the layers are unique. The interlayer coherence is not destroyed in this GO sample.

HRTEM images were recorded at the edge of graphene oxide sheet, a region where the images could exhibit more details without the disruption of the overplayed sheets. From Figure 2.16 (c), it can be found from the edge of the graphene oxide sample, that the sample was consisted two layers. Form these images, some defects and disorder on the graphene oxide surface can also be observed. Figure 2.16 (d)
shows that, the sample were consisted of two layers, and compared with Figure 2.16 (c), the lattice structures shown within the image appear clearer and suggest that defects or disorder also appeared. Additional HRTEM images of graphene oxide are presented in Appendix v, Figure B.3.

In summary, the TEM images coupled with SAED and HRTEM imaging provide detailed surface morphology information on the inner structure of the graphene oxide synthesised. The measurements reported hereby provide direct evidence on the formation of graphene oxide nanomaterials and its possibility for further functionalisation.

2.2.5.2. Raman spectroscopic characterisation of GO

![Raman spectrum of graphene oxide](image)

Figure 2.17 Raman spectrum of the graphene oxide synthesised.

Raman spectroscopy is a very powerful characterisation tool suited to identify the number of layers in graphene\textsuperscript{11,12} as well as to characterise the chemical and structural damages in it\textsuperscript{13,14,15}. Figure 2.17 shows a typical Raman spectrum of graphene oxide recorded during this work.
The spectrum display two prominent peaks at 1345 \( \text{cm}^{-1} \) and 1590 \( \text{cm}^{-1} \) along with two second order peaks at 2702 \( \text{cm}^{-1} \) and 2931 \( \text{cm}^{-1} \). The peak at 1345 \( \text{cm}^{-1} \) can be assigned to the D band. The D band was due to the surface defects, the disorder in the sp\(^2\) bonding, layer overlapping and appearance of other functional groups or graphited particles. The intensity of D band also reflected the degree of disorder of the graphitic structure within the measured graphene oxide. The peak at 1590 \( \text{cm}^{-1} \) was related to G band, which was characteristic of all graphitic structures, arising due to the in-plane bond-stretching motion of sp\(^2\) hybridised carbon atoms. The range after 2500 \( \text{cm}^{-1} \) was assignable to secondary order peaks, whereas the peak at 2702 \( \text{cm}^{-1} \) was the 2D peak, which was emergent the process whereby the momentum conservation was satisfied by two phonons with opposite wave vectors. For a perfectly single layer of graphene without any defects, the 2D band should be intense and sharp. In this newly synthesised graphene oxide batch, the broader 2D peak indicated that the area few layered graphene/graphene oxide structures. This is also in agreement to the HRTEM and SAED results. The peak around 2930 \( \text{cm}^{-1} \) is a combination mode of G and D bands, referred to as the D + G band. This is due to the combination of phonons with different momenta around K and \( \Gamma \) and consistent with previous literature reports.\(^{14}\)

The emerging of all D and G peaks confirmed the generation of graphene oxide, and clarified its characteristic structure. The 2D and D + G band also indicated that the properties of the synthesised graphene/graphene oxide reported hereby was unique and only a few-layered structure. The process was repeated as least 3 times and a degree of batch-to-batch repeatability was obtained.
2.2.5.3. FTIR spectroscopic characterization

FTIR characterisation was carried out to identify the chemical bonds appeared on the graphene oxide sheet. Figure 2.18 shows a typical FTIR spectrum. The broad transmittance peaks from 1800 cm$^{-1}$ to 2200 cm$^{-1}$ were the signals from the diamond detector.

![FTIR spectrum of graphene oxide](image)

**Figure 2.18:** FTIR spectrum of graphene oxide.

From the FTIR spectrum, several peaks give the evidence of chemical band appearing in this as-made graphene oxide material: the broad band at 3430 cm$^{-1}$ corresponding to O-H stretching vibration, the band at 1730 cm$^{-1}$ due to the C=O stretching from carbonyl and carboxylic groups, the 1589 cm$^{-1}$ band due to the skeletal vibrations of non-oxidised graphitic domains, the band at 1220 cm$^{-1}$ which is related to the C-OH stretching vibration and the band around 1090 cm$^{-1}$ due to the C-O stretching vibration. So, the FTIR date indicates the presence of the different types of oxygen functionalities and the oxygenated defects onto the graphene oxide surface.
2.2.5.4. Ultraviolet-Visible Spectroscopy

![UV-Visible Spectroscopy Graph](image)

**Figure 2.19:** UV-vis spectrum of an ethanol solution of graphene oxide (0.5 mg/mL).

The UV-vis characterisation of graphene oxide was carried out in order to study the light absorption capability of the synthesised graphene oxide sample. It has been reported that the graphene oxide can be dissolved in range of organic solvent and also in an aqueous phase. In our case, ethanol was chosen due to the relatively high ability to dissolve both graphene oxide (with sonication and centrifugation) and the applied porphyrin molecules (described in the following Chapters). The UV-vis spectrum shown in the Figure 2.19 is representative of the synthesised batches of GO reported hereby.

It can be seen from Figure 2.19 the graphene oxide solution exhibits a main absorption maximum at 230 nm and a secondary absorption band at 301 nm. The first one corresponds to a π-π* transition, due to the C-C aromatic bond; the secondary absorption peak at 301 nm can be attributed to a n-π* transition of C=O bands. This secondary absorption peak also indicates the presence of the C=O groups and the disorder and surface defects on graphene, which confirmed the formation of graphene oxide.
2.2.6. Thermally reduced graphene oxide (TRGO)

In a recent work, thermally reduced graphene oxide obtained via an annealing progress has been reported. As described, the rapid increase of the temperature to a high temperature, usually around 1050 °C, could reduce the graphene oxide by reduction of the oxygen-containing groups. The annealing process to give the thermally reduced graphene oxide (TRGO) is dependent on the annealing temperature. In the measurements of volume electrical conductivity, the 500 °C reduced graphene oxide exhibits only 50 S/cm, while the 700 °C and 1100 °C reduced graphene oxides could reach to 100 S/cm and 550 S/cm.

Figure 2.20 Schematic representation of a thermal reduced graphene oxide (thermally reconstruction of graphene from reducing graphene oxide, double bonds were removed for clarity).

As the oxygen etching effects will dramatically increase when heating to a high temperature, the H₂ gas phase atmosphere are introduced to eliminate this reaction by consume oxygen. The added H₂ can rapidly consume the residual oxygen within the system. So, in this work, the thermally reduced graphene oxide was carried out by a rapid increase of heating temperature to 1050 °C, then the sample was maintained at this temperature for 2 hours. The annealing process was conducted under a hydrogen and argon atmosphere (1 : 9), in which hydrogen was used as the reductive agent. Figure 2.20 shows a schematic representation of thermally receded graphene oxide.
2.2.6.1. Spectroscopic characterisation by Raman spectroscopy

Figure 2.21: Raman spectra of graphene oxide and thermally reduced graphene oxide.

Figure 2.21 shows the Raman spectra of graphene oxide and thermally reduced graphene oxide. In the thermal reduction process, molecular hydrogen was introduced as the reducing agent and the high temperature annealing progress was used to repair the surface defects. The graphene oxide exhibits a D band at 1347 cm$^{-1}$ and a G band at 1594 cm$^{-1}$. The thermally reduced graphene oxide synthesised hereby presents a D band at 1350 cm$^{-1}$ and a G band at 1590 cm$^{-1}$. For the thermal reduced graphene oxide, both the D band and G band are slightly red-shifted. This red-shift in the bands indicates that the functional groups in the surface have changed, due to the removal of the oxygenated groups. The calculated I$_D$/I$_G$ ratio for the graphene oxide is 0.91 while for the thermal reduced graphene oxide is 0.82. This decrease of I$_D$/I$_G$ ratio confirmed the repair of the defects and disorders in the graphene oxide surface. In addition, it can be also observed that both D band and G band for graphene oxide and reduced graphene oxide are relatively board, which indicates presumably a multi-layered structure in both materials.
2.2.6.2. Solid state investigation by Transmission Electron Microscopy (TEM)

TEM and HRTEM microscopy were applied in order to characterise morphologically the synthesised thermally reduced graphene oxide. Figure 2.22 (a) and (b) show that the reduced graphene oxide was still sheet like structures and, compared with graphene oxide, the area size of the sheets was around 2 micrometres.

Figure 2.22: (a) TEM micrograph of thermally reduced graphene oxide, scale bar = 1 μm (b) magnified TEM micrograph of thermally reduced graphene oxide, scale bar = 200 nm (c) HRTEM micrograph of thermally reduced graphene oxide, scale bar = 10 nm and (d) HRTEM micrograph of thermally reduced graphene oxide, scale bar = 5 nm.
The image also shows that the thermally reduced graphene oxide sheets can vary in size. “Wrinkles” are also observed on the surface of reduced graphene oxide sheets and such features seem to suggest emergence of defects. The thermal reduced graphene also shows different contrasting layers in TEM, which may be due to a different number of carbon layers across the specimen. After the thermally reduction, it can be found that the obvious defects and disorder on the sheets were successfully removed. (Additional TEM micrographs of the thermally reduced graphene oxide are provided in Appendix viii, Figure B.7).

Figure 2.22 (c) and (d) show the HRTEM micrographs of thermally reduced graphene oxide at different magnifications. From the micrographs the lattice structure can be clearly observed. The different orientations observed indicate the tendency of sp² structure was being presented. Also it indicated the presence of a multi-layer structure. From the micrographs the interplanar spacing of the thermal reduced graphene oxide was calculated, around 0.321 nm, (Figure 2.22 (d)), which corresponds to the (002) crystallographic planes of graphitic carbon, indicating the formation of graphene sheets. (Additional HRTEM images of thermal reduced graphene oxide are provided in Appendix vi, Figure B.4).

The TEM and HRTEM data of representative samples of the thermally reduced graphene oxide confirm that the reduction reaction occurred and led to formation of graphene sheets. After the thermal reduction process, the defects and disorders initially formed on the graphene oxide surface were minimised.
2.2.7. Chemically and microwave-based reducing of graphene oxide

As it has been reported,\textsuperscript{10} for a colloidal dispersion of graphene oxide a range of chemicals can be used in order to carry out a reduction process. Hydrazine hydrate was used initially and it is one of the most widely investigated chemical reducing agents use for the chemical reducing progress.\textsuperscript{21} The reaction was carried out heating a hydrazine and graphene oxide mixture on an oil bath at 100 °C over 24 hours. The benefit of this chemically reduction process is that the reaction could take place at relatively low temperatures. The thermally annealing process was also used to repair the surface defects of graphene oxide and aid the generation of synthetic graphene on a laboratory scale.\textsuperscript{17} In this case, an alternative heating source was used, microwave irradiation, which was applied to reduce graphene oxide.\textsuperscript{22,23} The main advantage of the use of microwave irradiation is that the heating occurs in a uniform manner and rapidly.

In this work, a novel cross-linking reaction was designed, which combines the chemical reduction process and microwave irradiation in order to reduce the synthesised graphene oxide samples. Hydrazine was used as the reducing agent, assisted with the microwave irradiation as the thermally annealing heating source. The combination of these two methodologies show clear advantages with respect to commercial methods, as the reduction reaction is completed in less time and the quality of the reducing material can be improved.
2.2.7.1. Spectroscopic characterization by Raman spectroscopy

![Raman Spectra](image)

**Figure 2.24:** Raman spectra of chemically and microwave-based reduced graphene oxide and graphene oxide.

Raman spectroscopy was carried out in order to analyse the inner structure of reduced graphene oxide and compares with the starting GO material, and to identify their graphitic sp$^2$-bonded extended aromatic carbon structure. From Figure 2.24, it can be seen that graphene oxide exhibited a D band at 1346 cm$^{-1}$ and a G band at 1599 cm$^{-1}$, the calculated $I_D/I_G$ ratio of starting graphene oxide was 0.83. The chemically and microwave-based reduced graphene oxide exhibited a D band at 1350 cm$^{-1}$ and a G band at 1596 cm$^{-1}$, and the calculated $I_D/I_G$ ratio of reduce graphene oxide was 0.80. As it can be seen from the measured results, both the D band and G band of reduced graphene oxide were slightly shifted and the $I_D/I_G$ ratio of reduced graphene oxide decreases from 0.85 to 0.80 compared to graphene oxide. This suggests the elimination of some of the defects and the increasing of the sp$^2$ carbon bonded structure indicating that reduction reaction occurred.
2.2.7.2. Solid state investigations by TEM and HRTEM microscopy

**Figure 2.25:** (a) TEM micrograph of a chemically and microwave-based reduced graphene oxide, scale bar = 200 nm, (b) magnified TEM micrograph of a chemically and microwave-based reduced graphene oxide, scale bar = 500 nm, (c) HRTEM micrograph of chemically and microwave-based reduced graphene oxide, scale bar = 5 nm and (d) HRTEM micrograph of a chemically and microwave-based reduced graphene oxide, scale bar = 5 nm.
The TEM and HRTEM imaging were carried out to study the surface morphology and the lattice parameters of the chemically and microwave-based reduced graphene oxide sample.

Figures 2.25 (a) and (b) show the TEM micrographs of chemically and microwave-based reduced graphene oxide. The reduced graphene oxide has a sheet-like morphology and the sizes of the sheets are in the micrometre range. This is similar to that found in the as-made graphene oxide and thermally reduced graphene discussed above. “Wrinkles” are also generated on the surface of graphene oxide sheets and these may be limited to the presence of local defects. In addition, the chemically and microwave-based reduced graphene presents more overlaid wrinkles compared with the thermally reduced graphene oxide, possibly due to the use of a more aggressive reaction conditions. Although there are more wrinkles, the chemical defects and disorders are significantly removed in the reduction process (Additional TEM images of chemically and microwave-based reduced graphene oxide are presented in Appendix ix, Figure B.8).

HRTEM images of chemically and microwave-based reduced graphene oxide are shown at Figure 2.25 (c) and (d). The lattice structure of the chemically and microwave-based reduced graphene oxide can be observed from HRTEM images. Similar to the case of the thermally reduced graphene oxide, the different lattice orientations indicate that the sp² structure is maintained and also indicate a multi-layer structure. From the calculated lattice parameters, shown in Figure 2.25 (d), the interplanar spacing of chemically and microwave-based reduced graphene oxide is around 0.321 nm, corresponding to the (002) crystallographic planes of graphitic carbon, this is a strong evidence towards the formation of graphene sheets. Compared with the thermally reduced graphene oxide, the chemically and microwave-based reduced graphene oxide presented a lesser degree changes in the interplanar spacing, which means the number of layers presented in the sample of chemically- and
microwave-based reduced GO was slightly less than that formed for thermally reduced graphene oxide. (More HRTEM images of chemically and microwave-based reduced graphene oxide are presented in Appendix vii, Figure B.5).

Both TEM and HRTEM results of chemically and microwave-based reduced graphene oxide established that the hydrazine hydrate and ammonia, especially in the microwave assisted process for the reduction reaction, are effective for the generation of graphene sheets. After the thermally reduced process, the defects and disorders on the graphene oxide surface are removed. Compared with the thermally reduced graphene oxide, the chemically and microwave-based reduced graphene oxide presents a smaller number of sheets. Therefore, it would be of interest for generating more tailed made graphene-analogues in a synthetic manner.

2.2.7.3. Solid state investigation by SEM microscopy

The SEM characterisation was carried out in order to obtain information about surface morphology in a larger scale (μm) than the TEM (nm). The EDS analysis together with SEM was carried out to analyse the elemental composition of the graphene oxide sheets (see Figure 2.26), which will help to identify the degree of reduction for the graphene oxide sample. The EDS analysis results are shown in Table 1.
Figure 2.26: (a) SEM image of chemically and microwave-based reduced graphene oxide, scale bar = 30 μm; coupled with EDX analyst.

From the SEM measurement, the image recorded suggested that the reduced graphene oxide still maintains the sheets like structure. The EDX analysis results in Table 1 showed that after the chemical- and microwave-based reduced treatment, the atom percentage oxygen (which accounts for the main defects and disorders present), are reduced to 4.7 %. The amount of oxygen stays at a lower level and indicates that the reducing reaction occurred as predicted. Other elements appeared in the table, like Na, Cl and S, are the residuals came from the synthesis process of graphene oxide.

Table 1: EDX analysis for a sample of chemically and microwave-based reduced graphene oxide.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>F</th>
<th>Na</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>77.11</td>
<td>16.97</td>
<td>2.40</td>
<td>0.05</td>
<td>2.17</td>
<td>0.10</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>95.25</td>
<td>4.71</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>97.16</td>
<td>2.70</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>97.10</td>
<td>2.81</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 5</td>
<td></td>
<td>27.26</td>
<td>41.07</td>
<td></td>
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</tbody>
</table>
2.2.8. Self-assembled hydrothermal reduced graphene oxide hydrogel

To build up a 3D characteristic structure of a hydrogel\textsuperscript{24}, a procedure based on the self-assembly of reduced GO was carried out. The graphene and graphene oxide of relevance have 2D structure, which reduces these materials with promising chemical and physical properties for hydrogels formation. The modification and functionalisation of graphene oxide as always been probed in this project. There, a hydrothermal treatment of graphene oxide was applied to build up a 3D network structure. Three-dimensional network structures obtained in the project so far showed a long list of beneficial properties including: macroscale size, high accessible surface area, less aromatic restacking, highly-interconnected microstructures, high strength and flexibility suitable properties for a fast ion transport and electronic conductivity.\textsuperscript{25} The relatively high temperature and high pressure needed to generate the hydrogel also were contributed to the reducing and exfoliation of the graphene oxide, to generate reduced graphene oxide in a one-step process. The generation of the 3D structure also provided an alternative way to generate a novel graphene oxide composite. In this project, the synthesis published earlier was adapted by adding 0.5 mg/mL graphene oxide water solution into an autoclave. The reaction was then carried out at 200 °C over 24 hours. The pressure generated within the autoclave used can up to 1800 psi, generating the desired hydrogel of RGO upon competition (See Experimental Section for details)
2.2.8.1. Raman spectroscopic characterisation

![Raman spectrum graph](image)

**Figure 2.27:** Raman spectrum of hydrothermal reduced graphene oxide, assembled into the 3D hydrogel.

In order to identify the inner structure of the resulting self-assembled reduced graphene oxide (rGO), Raman spectroscopy investigations were carried out, using the 830 laser excitation. As shown in Figure 2.27, the Raman characterisation was accessed to compare the spectroscopy of graphene oxide and self-assembled, hydrothermally reduced graphene oxide. In spectra recorded, both graphene oxide and the self-assembled, hydrothermally reduced graphene oxide showed relatively broad D band and G band. These were due to their multi-layered structure. Raman spectrum of GO showed a D band at 1350 cm\(^{-1}\) and a G band at 1592 cm\(^{-1}\). The \(I_D/I_G\) ratio of graphene oxide before the hydrothermal reduced process was 0.91. This is only slightly higher than that of the self-assembled reduced graphene oxide obtained after the hydrothermal reduction, which presented a D band at 1349 cm\(^{-1}\) and a G band at 1603 cm\(^{-1}\), whereby the \(I_D/I_G\) ratio was 0.84.

Compared with the case of graphene oxide, the G band of self-assembled reduced graphene oxide obtained was red-shifted, hereby from a 1592 cm\(^{-1}\) in the former to 1603 cm\(^{-1}\) in the latter material. This red-shifted G band indicates the
successful removal of some of the functional oxygenated groups typically formed on the surface of graphene oxide. The $I_D/I_G$ ratio of the self-assembled reduced graphene oxide material decreased from 0.91 to 0.84, which indicated that the self-assembled reduced graphene oxide is likely to have a better, less defects, extended graphitic $sp^2$ structure than the graphene oxide. This somewhat decreased $I_D/I_G$ ratio suggested that the reduction of graphene oxide occurred after the high pressure and mildly high temperature applied. As described Raman spectroscopy, the hydrothermal reaction under these conditions could lead to self-assembled hydrothermally-reduced graphene oxide which involved the partial reduction of graphene oxide in a one-step process. However, the degree of reduction and specific removed of oxygenated groups would need further analysis for a precise conclusion to be obtained.
2.2.8.2. Solid state investigation by SEM

![SEM images of self-assembled graphene oxide](image1)

![SEM images of self-assembled graphene oxide](image2)

![SEM image of starting material GO](image3)

**Figure 2.28:** SEM images of self-assembled graphene oxide, (a) scale bar =100 μm (b) scale bar =10 μm; (c) SEM image of starting material GO, scale bar = 10 μm

SEM measurements were introduced to obtain the surface morphology information of hydrothermally reduced graphene oxide gel and compare these with the morphology of the starting materials. In order to fully understand the three dimensional structure of hydrothermal reduced graphene oxide gel without any damage to the surface, the SEM sample was prepared under freeze drying conditions to remove all the solvent absorbed into the porous 3D structure characteristic to hydrogels.

Figure 2.28 shows the results of the measurement. From Figure 2.28 (a), the
morphology of the hydrothermal reduced graphene oxide gel can be clearly seen that the gel has a stable 3D structure in the solid state. The magnified SEM image displayed more surface details. After the hydrothermal reduced process, the graphene oxide starting material self-assembled to form a micro-porous network structure. The pore walls are made of the reduced graphene sheets. It can be observed that the hole size of the hydrothermal reduced graphene oxide hydrogel is around 2 μm to 5 μm and the pore size of this 3D structure are rather separated in space. The high temperature and pressure reaction condition resulted in the graphene oxide sheets (converting, overlapping and coalescing to from those cross-links) give rise to the framework of the designed graphene hydrogel. As described in SEM images, the large conjugated carbonaceous planes make the reduced graphene sheets rather stiff and able to give the stable network. This can be potentially functionalised and used as a synthetic scaffold to other functional materials. Overall, the SEM measurement of the hydrothermal reduced graphene oxide hydrogel allowed a direct visualisation of the 3D structure and its comparison with the GO starting material.

2.3. Conclusion to Chapter 2

In this chapter, we first explored the possibility of obtaining surface-oxidised SWNTs by applying strong acids techniques using adaptive of four literature methods. The results oxygen containing groups can be introduced onto the surface in a controlled way. The drawbacks of the oxidation process were that the structure of SWNTs were hugely damaged, which was confirmed by TEM and Raman. The tailor made purification of commercially-available SWNTs was carried out to remove target impurities. In this project, a microwave step was introduced in the purification procedure. The acid wash purification was combined with the microwave technique to afford a multi-step purification process. Whilst the multi-acid wash purification process could remove most of the impurities, due to the rather complicated process and strong reaction conditions, the yield of this method was relatively low and the structure of SWNTs were also significantly damaged, as shown by Raman
investigations. The steam purification process was introduced as an alternative, to remove amorphous carbon within an annealing process. In this method, steam was used as a mild oxidising agent, since the previous purification generated too many defects in the structure of SWNTs. The process does remove some of the impurities, mainly the carbon layers wrapping the metallic catalytic nanoparticles, but the Raman spectra still indicated the presence of a high degree of defects at the same time. Next, the Bingel reaction was also carried out on the modified SWNTs surface. The Bingel onto reaction modified SWNTs still showed an intact sp$^2$ carbon bond structure and the attached groups were further converted, rendering their materials ready to be used as a linking bridge to other molecules. This further functionlisation will be discussed in Chapter 4.

The synthesis of graphene oxide was also described in this chapter, basing on an adapted methods form the literature. Graphene oxide was synthesised by exfoliating from graphite oxide in liquid phase with a prolonged sonication time, which is a modification from literature$^{10}$. The light absorption property of graphene oxide was studied by UV-vis spectroscopy. Raman spectroscopy was also used to investigate the inner structure of the graphene oxide obtained. To reduction of graphene oxide was addressed by a chemical reduction method, techniques as well as by a thermal reduction method. The chemically reduced graphene oxide obtained was resulted by using hydrazine as a regent and microwave technology. Raman spectroscopy, TEM and HRTEM together suggested that reducing reaction proposed occurred. The thermally reduced graphene oxide was obtained by a high temperature and molecular H$_2$ reduction reaction. The hydrothermal reduction was applied to give a one-step self-assembled graphene oxide material with a 3D structure. The SEM images of this self-assembled hydrothermal reduced graphene oxide showed that this material was build-up of a porous network 3D with a hydrogel structure. This could become the basis of a promising graphene oxide composite generation strategy.
In summary, we applied hereby some modified methods for surface functionalisation and purification of SWNTs (provided by Thomas Swan) and the pathways of synthesis and reduction of graphene oxide (synthesised by adapted literature methods).

2.4. References to Chapter 2

Chapter 2 Results and Discussions


Chapter 3 Synthesis and Characterisation of a Metal Centred Functionalised Porphyrin

3.1. Overview

Inspired by the efficient energy transfer in naturally occurring photosynthetic reaction centres, various porphyrins\(^1\) and phthalocyanines\(^2\) have been synthesized and applied in several examples of dye-sensitised solar cells and related photovoltaic devices. Porphyrins constitute a large class of naturally occurring intensely coloured, red or purple, macrocyclic pigmented compounds. As a group of heterocyclic macrocycle organic compounds, porphyrins are composed of four modified pyrrole subunits interconnected at their \(\alpha\) carbon atoms via methine bridges. Porphyrins, as planar, electron-rich, aromatic materials, are characterised by remarkably high extinction coefficients in the visible region. They have already been used in some recent studies as chromophores having the ability to act as dispersing agents and to decorate carbon nanotubes\(^3,4,5\) and nanohornes\(^6,7\) for the development of artificial photosynthetic devices\(^8\).

One of the most common and simple free base porphyrins is \textit{meso}-tetraphenylporphyrin. For this, the synthetic strategy was a condensation and oxidation reaction starting with pyrrole and aldehyde. In this project, the synthetic pathway for the free base porphyrin was carried out on a laboratory scale by modifying an old literature procedure which gave the analytical scale synthesis (normally the final yield of porphyrin generation is less than mg, start from 10g) of such porphyrin.\(^9\) Compared with the commercial \textit{meso}-Tetraphenylporphyrin, the synthesised free base porphyrin of interest has two aryl thioacetate-functionalised side groups at \textit{meso}-position, which can be used to further functionalise covalently linking by other designed functionalists. At the same time, the free base porphyrin also has
four hexyl chains at the $\beta$-position, which can be employed to increase the overall solubility. They are bulky and can generate space to separate individual molecules, to other materials, this was deemed an important design feature mediating the bonding with other small molecules, nanoparticles and nanotubes. Another supplementary reason for choosing a porphyrin with a grafted thioacetate-functionalised side group and four hexyl chains was the fact that the added linkers at $meso$-position or $\beta$-position may dramatically change or enhance the possible electron movement or injection ability from porphyrin molecule to nanoparticles present in the solar cells or photovoltaic devices designs.

In order to characterise the light absorption and emission properties of the newly synthesised free base porphyrin, UV-vis and fluorescence spectroscopy, including two-dimensional fluorescence contour plotting measurements were carried out. The solvent accessible surface electrostatics potential of free base porphyrin was studied based on a free base porphyrin crystal structure (Provided by Dr Sofia Pascu) by computational calculations.

The porphyrin core is a tetradeutate ligand with a maximum diameter of approximately 3.7 angstroms in which the available space is used to incorporate with metalation. In this project, the free base porphyrin was converted to a member of this family with substituted metal centre, which included Zinc(II), Indium(III) and Gallium(III). The metallation reactions were carried out in a microwave reactor. The Zn(II)-porphyrin was then selected to further evaluate its interaction with single-walled carbon nanotubes and graphene oxides (synthesised as described in Chapter 2). This Chapter provides the synthetic and spectroscopic details for the porphyrin starting material, and forms the basis of the porphyrin nanohybrid structure designed in Chapter 4.
3.2. Results and discussions.

3.2.1. General synthesis strategies of free base porphyrin

Figure 3.1: Schematic diagram of free base porphyrin generation.
The proposed synthetic route for the free base porphyrin, provided in a paper from 1999\(^9\) consisted of a series of condensations and oxidation reactions starting from 1-iodohexane, pentane-2,4-dione and benzyl acetoacetate, ideally devised for analytic scale work rather than laboratory scale, sustainable chemistry applications. The free base porphyrin was designed using two symmetry building blocks. The \(\beta\)-position of the free base porphyrin can be functionalised with carbon hexyl chains and further \textit{meso}-position be modified via aryl thioacetate-functionalised side groups.

![Chemical structure](image)

**Figure 3.2:** Step I-Synthesis of 3-Hexylpentane-2,4-dione.

3-Hexylpentane-2,4-dione (1) was synthesised \textit{via} an enolate substitution reaction using 1-iodohexane. The first reaction of the synthesis proved to be challenging. The reported procedure, even repeated more than 4 times, the final yield still didn't match the reported results. In the original reaction\(^9\), acetone was used as the solvent. Thus, during the reaction, dry acetone solvent and dried potassium carbonate were used. The reflux temperature for this reaction was set at 60 °C. The purification progress was carried out by using a fractional distillation. However, we observed that in fact this facilitated a side reaction where the acetone was converted to an enolate which reacted with the 1-iodohexane. As a result, contrary to the published report, multiple products were isolated and the yield of desired product was very low (\(< 5\%\)). The use of DMF was then employed, for the first time, in order to eliminate those side reactions. It also simplified the purification process and led to the formation of the desired product, compound 1, as described in the Experimental section.
Figure 3.3: Step II-Synthesis of 2-Benzyl-2-hydroxyimino-3-oxobutanoate.

This step relies on the fact that oximes can be synthesized by condensation of an aldehyde or a ketone with hydroxylamine or be obtained from the reaction of nitrites with compounds containing an acidic proton. In this case, for Step II, the synthesis of 2-Benzyl-2-hydroxyimino-3-oxobutanoate (2), a reaction of sodium nitrites with benzyl acetoacetate in acetic acid was carried out. In order to control the increase of the temperature (because of the exothermic reaction which is taking place by the addition of acetic acid), an ice/salt bath was used. The resulted compound 2 was then extracted by using diethyl ether and purification was carried out by washing the crude product several times with water, to remove the acetic acid. The yield of compound 2 was 87%.

Figure 3.4: Step III-Synthesis of benzyl1-4-(n-hexyl)-3,5-dimethypyrrole.
Chapter 3 Results and Discussions

For the synthesis of benzyl-4-(n-hexyl)-3,5-dimethylpyrrole (3), Knorr’s pyrrole synthesis was applied following an adapted method. Zinc dust and acetic acid were used as catalysts as described in the original procedure and the reaction was carried out by stirring overnight at 100 °C. The Knorr’s pyrrole synthesis first involves the condensation of a benzyl-2-hydroxyimino-3-oxobutanoate and a 3-hexylpentane-2,4-dione to give an imine, which further tautomerises to an enamine. This is then followed by cyclization, elimination of water, and isomerization to the final pyrrole. The addition of acetic acid was then added drop wise and zinc dust was added slowly over a 5 min period. After recrystallisation from methanol, the maximum yield of the desired compound, benzyl1-4-(n-hexyl)-3,5-dimethypyrrole, was 23%. The process was repeated several times, and this was found to be the best yield achievable for the gram scale.

![Figure 3.5: Step IV-Synthesis of benzyl-5-acetoxtmethyl-4-(n-hexyl)-3,5-dimethyl pyrrole.](image)

The synthesis of benzyl-5-acetoxtmethyl-4-(n-hexyl)-3,5-dimethyl pyrrole (4) was carried out via the benzyl-4-(n-hexyl)-3,5-dimethypyrrole (3). This was oxidised to the acetoxyethyl derivative by using lead tetraacetate Pb(OAc)$_4$ to oxidise one of the methyl groups found at the periphery of compound 3 and convert the methyl group to acyl protected reaction OH. Upon reaction, the solvent was removed under vacuum and the remaining mixture was dissolved in chloroform and filtered to remove any unreacted lead acetate. The remaining organic phase was then washed several times with water and dried over magnesium sulphate. The remaining solvent was removed under reduced pressure to afford an orange solid. This orange solid was
then recrystallised from methanol to afford compound 4 as a white solid. This step was repeated several times (least 5 times) under the conditions above, and the optimum yield of 17% was obtained.

![Diagram](image)

**Figure 3.6:** Step V-Synthesis of 5,5’-Dibenzyl-3-3’-di-(n-hexyl)-4,4’-dimethyldipyromethane.

The acid-assisted pyrrole dimerisation was applied to convert compound 4 to the 5,5’-Dibenzyl-3-3’-di-(n-hexyl)-4,4’-dimethyldipyromethane. This step was carried out in the presence of hydrochloric acid and under heating to reflex. The acidic environment and high temperature drove the reaction. The reaction finished with a red oily material. The final product was recrystallised from this oil using methanol, with a final yield of 14%.

![Diagram](image)

**Figure 3.7:** Step VIII-Synthesis of α-bromo-m-tolylaldehyde.

For the inclusion of the side group, the α-bromo-m-tolylaldehyde was first obtained by the DIBAL-H reduction of nitrile to aldehyde. In this reaction, α-bromo-m-tolunitrile was used as the starting material. Unlike the common reductant
NaBH₄, where NaBH₄ is considered a “nucleophilic” reductant as it delivers hydride (H-) directly to a carbonyl carbon, the mechanism involved at the reduction by DIBAL involves an “electrophilic” reductant. The first step in the reaction relies on the coordination of a lone pair from the carbonyl oxygen (a nucleophile) to the aluminium centre (electrophile). After coordinating to its carbonyl host, DIBAL delivers its hydride to the carbonyl carbon, resulting in the formation of a neutral hemiacetal intermediate that is stable at the low temperatures which are generated by the ice bath used in the process. Afterwards, the quenching of the reaction breaks down the hemiacetal, resulting in the isolation of the aldehyde. The by-product, of this reaction could be aluminium salts and ammonia, with high thermodynamic stability during the reaction forward. The solvent was then removed and recrystallised from petroleum ether under -18 °C to afford white crystals. The reaction was repeated at least 3 times, to that the highest achievable yield is reported: the final yield was 78%

![Figure 3.8: Step IX-Synthesis of 3-(S-acetylthiomethyl)benzaldehyde.](image)

For this step, potassium thioacetate was introduced into the conversion reaction of the side group. The reaction processes typically used to convert benzylic halides to thiols normally involves two different steps. Firstly, the initial substitution of halide by a thioacetate group leads to form anion of the thioesters. Secondly, the thioesters can be de-protected by basic or acidic deacetylation to form the thiols. In free base porphyrin synthesis, in order to avoid the reduction of the thiol groups to from by-products, such as R-S-S-R during the macrocycle ring formation, the modification of the side groups were stopped hereby to the substitution of halide by thioacetate group to generate 3-(S-Acetylthiomethyl)benzaldehyde, and there was no
de-protection of the –SOAc group. The purification of compound 9 was carried out by column chromatography and the final optimised yield was 87%.

Figure 3.9: Step VI, VII, X-Final assembly of free base porphyrin (10).
Chapter 3 Results and Discussions

For the synthesis strategies involved in steps VI, VII, X leading to the conversion of compound 5 to final the free base porphyrin (10), (5,15-Di(3-acetyltiophenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin), the reactions were carried out in one-pot without further purification and characterisations of the intermediates 6 and 7 due to the high reactivity.

The de-protection and hydrogenation of Compound 5 was carried out by dissolving compound 5 in THF (containing 1% Et₃N) and the mixture was then degased by nitrogen and vacuum. After this step, the palladium on carbon was added into the mixture and leaved to react under an atmosphere of hydrogen likely to afford compound 6, which was not isolated. Then, compound 6 was acid catalysed, leading to the decarboxylation under Trifluoroacetic acid (as Lewis acid catalyst) likely to afford compound 7. Compound 9 was then dissolved in methanol and added into the mixture compound 7 solution by cannula. To this, a stoichiometric quantity of DDQ was then added in order to oxidise and stabilise the porphyrinogen into the corresponding free base porphyrin, compound 10. Then triethylamine (Et₃N) was added dropwise to quench the reaction mixture, and then the solvent was removed under reduced pressure. The residue was then re-dissolved in CH₂Cl₂ and washed with water, dried over sodium sulphate, filtrated and passed through a plug of silica gel. Column chromatography was used to afford compound 10 which after this purification could be obtained with an optimised yield of 12%. The purified compound 10 was characterised, and identity confirmed by 500Hz ¹H NMR, ¹³C NMR spectroscopy as well as COSY and HMQC NMR techniques with the assigned peaks corresponding to each of the functional groups. Mass spectrometry measurements were also carried out. Due to aggregation, only MALDI techniques proved helpful in charactering this compound, nevertheless its identity could be fully confirmed.
Figure 3.10: (a) $^1$H NMR spectrum and (b) $^{13}$C NMR spectrum of free base porphyrin.
Figure 3.11: (a) COSY NMR and (b) HMQC NMR of free base porphyrin.
3.2.1.1. Solvent accessible surface electrostatics potential

Figure 3.12: (a) Free base porphyrin cell packing diagram, view over axis \( a \), crystal structure was obtained by Dr Sofia Pascu, (b) Solvent accessible surface electrostatics potential of packed cell structure of figure a.

A single crystal of this compound was grown with the assistance of Dr Sofia Pascu. Compound 10 crystallises in the Triclinic system, P-1 space group, with two non-symmetrically equivalent molecules in the unit cell (Figure 3.12 a). Structural data, selected bond lengths and angles and hydrogen bond tables are provided in the Appendix D. The solvent accessible surface electrostatics potential was investigated by a computer calculation based on the free base porphyrin crystal structure which was obtained by Dr Sofia Pascu. The free base porphyrin molecules are oriented face-on and show two heptane chain groups placed anti with respect to the aromatic core. Thus, the free base porphyrin shows a 3D supramolecular structure in the unit cell, which also shows weakly linked tubular arrangements in the solid state. Electrostatic potential correlates with dipole moment, electronegativity, and partial charges and the study of solvent accessible surface electrostatics potentials provided a visual method to understand the relative polarity of the free base porphyrin molecule.
The program used for this data visualisation and manipulation was Marvin Space.

As shown in Figure 3.12, the calculated partial charges may be represented as spheres, which show how the molecule would interact with approaching protons or positive charges. The red colour was used to present the negative electrostatic potential, which corresponds to an attraction of the proton by the concentrated electron density in the free base porphyrin molecule, while, the blue colour was used to exhibit the positive electrostatic potential. This corresponds to the repulsion of the proton by the atomic nuclei in the regions of free base porphyrin molecule where low electron density exists and the nuclear charge is incompletely shielded.

The calculation of free-base porphyrin crystal structure electrostatics potential suggests that the differences between the red and blue colour may be assignable to the aryl thioacetate side group functionalities and hexyl chains. The other parts of the free base porphyrin are represented in the white colour, which means that after functionalisation, the free base porphyrin molecule can allow more non-polar solvent gain access to its surface. The relatively non-polar surface enhances the free base porphyrins’ solubility in more common solvents, e.g. toluene, chloroform and ethanol, which is necessary for the formation of hybrids with hydrophobic nanomaterials such as carbon nanotubes and GO. The calculated result also agrees with the original design and was deemed appropriate for further synthesis strategies to give nanomaterials.

3.2.1.2. Ultraviolet-visible spectroscopy of free base porphyrin

The Ultraviolet-visible (UV-vis) spectroscopy measurements on compound 10 were carried out to investigate the light absorption behaviour of this free base porphyrin in a common solvent (ethanol). The measurements show that the Soret band, the wavelength of maximum absorption of this free base porphyrin occurs at 411 nm, which is in the blue visible region. This is due to the electron dipole movement that
allows the $\pi-\pi^*$ transition. Beside the main maximum light absorption band, the free base porphyrin also exhibited several secondary absorption bands at 508 nm, 542 nm and 574 nm. The light absorption behaviour of free base porphyrin indicates that the free base porphyrin can absorb visible light energy and then potentially convert this energy into electron excitation, which can be used as light harvesting unit in photovoltaic devices.

![Absorbance spectrum of free base porphyrin](image)

**Figure 3.13**: UV-Vis spectroscopy of free base porphyrin (Concentration: 1 $\mu$M in ethanol).

The understanding of free base porphyrin light absorption behaviour is necessary as this compound is of interest as a light harvesting molecule. This spectrum presents in further will compare with its metallated porphyrin and the free base porphyrin@carbon nanomaterial hybrids.

### 3.2.1.3. Two-dimensional fluorescence contour plotting free base porphyrin and its derivative.

Two-dimensional fluorescence contour plotting measurement of the free base porphyrin was used to investigate the fluorescence behaviour of free base porphyrin
(when tests, was dissolved in ethanol at 1μM). Several different solvents were investigated, depending on the subsequent experiments requirement. As such toluene or chloroform can also be used in future experiments. The two-dimensional fluorescence contour plotting was recorded under λ excitation (recorded every 10 nm) from 200 nm to 800 nm and collecting the λ emission from 200 nm to 800 nm (scanned every 10 nm) respectively. As for the measurement results, a strong emission region were observed from 590 nm to 700 nm and the free base porphyrin ethanol solution (1μM) exhibited strong fluorescence emission when excited by λ excitation 250 nm to 400 nm and from 450 nm to 600 nm. The excitation light wavelength also corresponding with the observation from UV-vis measurements: under the Soret band and three secondary absorption bands, the free base porphyrin exhibits strong fluoresces behaviours as consistent with literature report.\textsuperscript{12} The 2-dimensional fluorescence mapping also indicated that the free base porphyrin can absorb a large range of input visible light energy, which is a desirable feature for a light harvesting molecule unit.

![Two-dimensional fluorescence contour plotting of free base porphyrin.](frame-3.14)

*Figure 3.14:* Two-dimensional fluorescence contour plotting of free base porphyrin.

(Concentration: 1 μM in ethanol)
3.2.2. General synthesis strategies for metalation of free based porphyrin (compound 10)

![Figure 3.15: Schematic diagram of the Zn(II) metalloporphyrin (compound 11) generation.]

The size of the free base porphyrin-macrocycle is perfectly suited to bind almost all first row transition metal (TM) metal ions and indeed a large number of main group metals. These can be inserted in the centre of the macrocycle forming metalloporphyrins. The metalated porphyrins are of significance for several different biochemical and photovoltaic chemistry, given their central role in light harvesting, photosynthesis, oxygen transport and in various redox reactions.\(^\text{13}\) During the metallation reaction, when the metal ion \(M^{n+}\) is incorporated into the free porphyrin (H\(_2\)P) core to form MP\(^{(n-2)+}\), the two amine protons in free base porphyrin are dissociated from the two pyrrole groups as shown by the following equation:

\[
M^{n+} + H_2P = MP^{(n-2)+} + 2H^+.
\]

Depending on size charge and spin multiplicity, metal ions (e.g. Zn, Cu, Ni, Co, etc.) can fit into the centre of the planar tetrapyrrolic ring system forming regular metalloporphyrins resulting in a kinetically inert complexes. Zinc, Indium and Gallium were chosen hereby for the metalation step of this project due to the fact that the resulting dye molecule could play promising for performance in solar cells design.\(^\text{14}\)
The general procedures for porphyrin Zinc metalation was applied by a treatment with excess \( \text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O} \) in chloroform at room temperature with gentle heating and under stirring. To enhance the reaction yield, in this project, as an adapted synthetic method from the general known metalation technique was used. Zinc acetate and compound 10 were mixed in a DMF solution and then the mixture was treated held for 10 minutes under the microwave, in a Biotage reactor at 150 °C. After purification, the final yields were very high, optimised at around 80%, which is significantly higher and also a faster procedure than conventionally. Figure 3.16 shows the \(^1\text{H} \) NMR of the resulting Zn(II)-porphyrin (Compound 11). Figure 3.17 also presents the comparison of the \(^1\text{H} \) NMR spectroscopy of the free base porphyrin (compound 10) and Zn(II)-porphyrin (compound 11). It can be founded that, after metalation, the NH peak of compound 10 disappeared entirely.

**Figure 3.16:** \(^1\text{H} \) NMR of Zn(II)-porphyrin (Compound 11) in DMSO.
Chapter 3 Results and Discussions

Figure 3.17: $^1$H NMR of free base porphyrin (in Chloroform) and Zn(II)-porphyrin in (DMSO).

3.2.2.1. Two-dimensional fluorescence contour plotting fluorescence imaging characterisation of free base porphyrin and Zn(II)-porphyrin

A two-dimensional fluorescence contour mapping was generated for the Zn(II)-porphyrin. This was needed to investigate the fluorescence behaviour of Zn(II)-porphyrin. (compound 11 was dissolved in ethanol at 1µM). And the two-dimensional fluorescence contour plotting was recorded under a $\lambda$ excitation ranging 200 nm to 800 nm and $\lambda$ emission from 200 nm to 800 nm respectively.
From the observed map, a strongly emissive region was observed from 570 nm to 670 nm. The compound 11 ethanol solution analysed exhibited strong fluorescence emission behaviour when excited from 200 nm to 400 nm and from 500 nm to 650 nm, which seemed to suggest that the compound 11 can absorb visible light over a large range. The maximum emission region occurred as expected from the UV-vis spectroscopy: the Soret band at 414 nm and secondary absorption band at 546 nm gave the maximum fluorescence emission behaviour. The two-dimensional fluorescence contour plotting measurement along with Ultraviolet-visible spectra measurement indicated strongly that the compound 11 synthesised could potentially be applied as a light harvesting molecule, and represents a promising building-block for photovoltaic devices.

3.2.2.2. Zn(II)-porphyrin fluorescence life time characterisation by single-photon fluorescence spectroscopy

To study the fluorescence decay behaviour of compound 11, 1 μM of the compound 11 ethanol solution was prepared and single-photon fluorescence lifetime spectroscopy was performed (λ_{ex} = 473 nm). The single-photon fluorescence decay
time profiles were shown in Figure 3.19, the fluorescence lifetimes of photo-excited compound 11 were fitted on a single component experiential function (τ = 100%) to give a lifetime of 6804 ps (6.8 μs) using SPCImage programme. The fitted curve corresponds to a $\chi^2 = 1.22$, which indicate a rather low error in the measurement and the resulting 6804 ps lifetime was reliable for a porphyrin.

![Figure 3.19](image)

Figure 3.19: Single-photon fluorescence lifetime spectroscopy of Zn(II)-porphyrin ($\lambda_{ex} = 473$ nm, Zn(II)-porphyrin 1 μM disperse in ethanol).

The single-photon fluorescence lifetime spectroscopy gives a direct insight into fluorescence decay rate and the Zn(II)-porphyrin exhibits a relatively long fluorescence lifetime, which is very useful for a light harvesting molecule. With this information in hand, it was decided that this parameter will be followed after the reaction with other materials, as a respective change in fluorescence lifetime could indicate the formation of nanohybrids or complexes structure, as these could induce subtle changes in the fluorophore’s environment.
3.2.2.3. Zn(II)-porphyrin single photon confocal fluorescence microscopy imaging

The sample preparation for solid state single-photon laser confocal fluorescence measurement involved drop-casting a solution of compound 11 onto borosilicate glass. A wavelength of $\lambda_{ex}=405$ nm was used to perform FLIM on the thin film. Figure 3.20 shows the measured results. The single photon laser confocal fluorescence measurement constitutes a new method to explore the behaviour of compound 11 as thin film, as it allows the analysis of the fluorescence properties of this film. From the results of this measurement, the intensity map shows the spatial variations in fluorescence emission. The lifetime mapping along with the corresponding fluorescence lifetime distribution curve, showing the predominant lifetime component ($\tau_1$) for compound 11.
Figure 3.20: Single-photon laser confocal fluorescence microscopy: (a) solid state Zn(II)-porphyrin, intensity image, the measured area is 30 μm × 30 μm (b) lifetime mapping and scale bar and (c) corresponding fluorescence lifetime distribution curve with life time mapping.

The blue structures shown in the lifetime mapping results were formed due to the compound 11 self-assembly together to form a tiny crystal on the glass. The other parts of the FLIM image, which are coloured in light red or orange, were microcrystalline aggregates of compound 11 on thin film. The lifetime recorded in the solid state thin film was 1910 ± 30 ps, and the FWHM (full width at half of the maximum) was 200 ps. The lifetime mapping also seems to suggest that due to the highly conjugated planar structure, compound 11 trends to be self-assembled together to form crystalline structures, of different sizes and morphology, and these have been proofed by FLIM, ranging from 2400-2900 ps. Interestingly, there have been a sharp decrease of FLIM in thin film with respect to solution measurement, and this is to be expected given, the strong self-aggregation and changes in environment for individual molecule when drop-costing onto glass.
3.2.2.4. Optimised Orbital energy level in gas phase

![Crystal structure of Compound 12 dimer](image)

**Figure 3.21**: Two highest occupied and lowest unoccupied molecular orbital of de-protected Zn(II)-porphyrin (compound 12) from gas phase DFT calculations.

Disulphide liked de-protected compound 12 was obtained by de-protecting Zn(II)-porphyrin, and then the de-protected porphyrin were self-assembled together to form the dimer. For the further understanding of electron density and molecular orbitals of Zn(II)-porphyrin, DFT calculations were performed to obtain a direct view into the equilibrium geometry and electronic structures for the frontier orbitals of the Zn(II)-porphyrins. The crystal structure of the above complexes were first optimised by B3LYP 6-31G(d,p), following the method of Holland et al with the assistance of Dr Rory L. Arrowsmith and Dr David González Calatayud, whereby an restricted spin approximation was used for the optimisation of the Zinc(II) complex due to its diamagnetic nature. The calculated electronic structures did not present negative frequencies, indicating that the optimized geometries are in the inclusive energy...
minima and the convergence was reacted.\textsuperscript{16} The DFT calculation applied hereby was based on the X-ray structure of the disulphide liked de-protected compound 12. (See Appendix D for X-ray structure).

**Table 3.1:** Energies and electronic occupancy of the highest occupied and lowest unoccupied molecular orbitals of the compound 12 from gas phase optimisations (DFT).

<table>
<thead>
<tr>
<th>MO</th>
<th>Occ</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO + 5</td>
<td>0</td>
<td>-0.26</td>
</tr>
<tr>
<td>LUMO + 4</td>
<td>0</td>
<td>-0.32</td>
</tr>
<tr>
<td>LUMO + 3</td>
<td>0</td>
<td>-0.50</td>
</tr>
<tr>
<td>LUMO + 2</td>
<td>0</td>
<td>-0.53</td>
</tr>
<tr>
<td>LUMO + 1</td>
<td>0</td>
<td>-1.86</td>
</tr>
<tr>
<td>LUMO</td>
<td>0</td>
<td>-1.87</td>
</tr>
<tr>
<td>HOMO</td>
<td>2</td>
<td>-4.82</td>
</tr>
<tr>
<td>HOMO – 1</td>
<td>2</td>
<td>-4.93</td>
</tr>
<tr>
<td>HOMO – 2</td>
<td>2</td>
<td>-5.90</td>
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<td>-5.94</td>
</tr>
<tr>
<td>HOMO – 4</td>
<td>2</td>
<td>-5.97</td>
</tr>
<tr>
<td>HOMO – 5</td>
<td>2</td>
<td>-6.09</td>
</tr>
</tbody>
</table>

Porphyrrins with D\textsubscript{4h} symmetry\textsuperscript{17} generally show energetically degenerate two lowest unoccupied molecular orbitals (LUMO+1, LUMO) and nearly degenerate two highest occupied molecular orbitals (HOMO, HOMO-1), as showed in Figure 3.22. Table 3.1 presents the energy level of each molecular orbital: -1.86 eV for LUMO+1, -1.87 eV for LUMO, -4.82 eV for HOMO and -4.93 eV for HOMO-1. The calculated energy band gap for compound 12 was 3 eV, which indicates the strong light absorption behaviour and promising potential photovoltaic properties, which may be
applied in the design of solar cells. Commercial dye molecules employed in DSSCs were normally having a band gap from 1 eV to 3 eV\textsuperscript{18}. This means that the functionalised porphyrin compound \textbf{12} matches the range and can be used in a real device generation. This project did give access to this material in a laboratory scale, as opposed to analytical scale, so this may open up possibilities for real application\textsuperscript{19,20}.

Together with the molecular orbital structure and the calculated energy levels, it was observed that after the modification at both \textit{meso}-positions and \textit{β}-positions with aryl thioacetate groups and introduced of long hexyl chains respectively, the electron-rich density areas were reported from the macrocyclic ring (shown in HOMO) centre towards the \textit{meso}-positions (as shown in LUMO) and \textit{β}-positions (as shown LUMO+1). Those results reveal that the substitutions at the \textit{meso}-positions and \textit{β}-positions of Zn(II)-porphyrin mainly affect the energy levels for unoccupied orbitals of the Zn(II)-porphyrin. Since the molecular orbitals involved the ligand framework (including the phenyl substituent) as well as the metal, it is very likely that they both contribute to the UV-vis light absorption properties. This could explain the observed similarity between the UV-vis absorption bands in this family of compounds, and the presence of a metal centre, as well as the nature of the metal, may all influence the spectroscopy properties.

Those modelling results also seem to suggest that after further interactions with other materials, such as carbon nanotubes, graphene oxide or reduced graphene oxide which may act as electron acceptors, the substitutions of the side groups and hexyl chains may play a significant role in determining fast electron injection from the excited singlet state of Zn(II)-porphyrin acting as a donor to other materials onto which this is absorbed, which could lead to variation in performance for an eventual PV device incorporating these.
3.3. Conclusion to Chapter 3

In this chapter, we demonstrated the lab scale (in porphyrin synthesis contest) synthesis of free base porphyrin, compound 10. The synthesis and purification procedure was modified and adopted from an older report which gives access to this material only on an analytical scale, to improve the final yield and allow the spectroscopic investigations. The structure of free base porphyrin were then characterised by NMR and mass spectrometry. For further understanding of the structure of the porphyrins, X-ray structures and DFT calculation are used and the solvent accessible surface electrostatics potential result indicate that in comparison with simple porphyrins which do not contain larger substitutions at the periphery designed thioacetate-functionalised porphyrin obtained better solvent solubility. The study of light absorption and emission behaviour of free base porphyrin was carried out by UV-vis and two-dimensional fluorescence contour plotting for the first time. From the UV-vis spectroscopy measurement results, the free base porphyrin (compound 10) has a strong Soret absorption band at 411 nm and secondary absorption band at 508 nm, 542 nm and 574 nm. The two-dimensional fluorescence contour plotting indicates free base porphyrin presented a strong emission regain from 590 nm to 700 nm.

Compound 10 was then metallated to generate Zinc, Indium and Gallium metalloporphyrin: Zn(II)-porphyrin (Compound 11), In(III)-porphyrin (Compound 11a) and Ga (III)-porphyrin (Compound 11b). The metallated porphyrins were obtained by microwave reactions, treating Compound 10 with the corresponding metal salt. The UV-vis spectroscopy measurement was carried out to identify the differences between each of the metalloporphyrins obtained. Among those three metalloporphyrins, Zn(II)-porphyrin (Compound 11) was deemed most appropriate for further measurements due to purity, yield and stability in solution and it has chosen for the next step, i.e. interactions with carbon nanomaterials. The FTIR spectroscopy indicated that expected functionalities are incorporated within the
compound 11 structure. The two-dimensional fluorescence contour plotting show that the compound 11 presented strong emission peaks from 570 nm to 670 nm. Both solution and solid state (thin film) single-photon fluorescence lifetime spectroscopy measurements were carried out to analysis the fluorescence lifetime. The solution single-photon fluorescence lifetime spectroscopy confirms that compound 11 exhibited relatively longer fluorescence lifetime which is around 6804 ps in ethanol (1 \mu M) and the solid state measurement results indicated the compound 11 thin film presented a 1910 ± 30 ps fluorescence lifetime in air phase. The DFT calculations (gas phase) of compound 12 were also carried out to study the orbital structure and energy level of compound 12. The calculated energy gap between HOMO and LUMO was 3 eV.

Overall, we have synthesised and characterised compound 10 and obtained in a satisfactory yield its corresponding metalloporphyrin for M = Zn(II). The light absorption and emission of compound 11 were studied in both solution phase and solid phase. The results obtained encourage that conclusion that the Zinc metalloporphyrin can be potentially applied as a light harvesting molecule for photovoltaic devices construction, and DFT calculations presented the HOMO-LOMO distribution.

3.4. References to Chapter 3


Chapter 4 Interactions Between an Aryl
Thioacetate-Functionalised Zn(II)Porphyrin and Single-Walled Carbon Nanotubes

4.1. Overview

Since single-walled carbon nanotubes were discovered by Iijima in 1993\textsuperscript{1}, the rigid rod-like tubular structure and highly delocalised extended $\pi$-electron system gives them unique electronic properties and renders them relevant for a variety of chemical transformations\textsuperscript{2,3}. Over the last 22 years, further studies have shown that by chemical functionalisation of SWNTs with small molecules and by using encapsulation techniques, it was possible to develop novel optoelectronic and photovoltaic devices.\textsuperscript{4,5,6,7} The interactions between fluorescent molecules and the aromatic surface of SWNTs have inspired an emerging area in which new nanohybrids materials have potential applications in solar cells\textsuperscript{8,9,10}. One of most attractive aspects of SWNTs chemistry remains the chemical modifications of their surfaces. SWNTs can be modified and, thus, functionalised by following a covalent or a non-covalent approach. The intrinsic $sp^2$ hybridised nature of the C-C bonding in SWNTs allows the reaction of the outer wall with organic molecules bearing specific functional groups and thus generating surface modifications. SWNTs can also interact via $\pi-\pi$ stacking with electron-rich planar molecules resulting in a supramolecular “donor-acceptor” adducts.

Porphyrins, as described in Chapter 3, are planar, electron-rich, aromatic species, characterised by remarkably high extinction coefficients in the visible region and have already been used in some recent studies as chromophores, which have the ability to act as dispersing agents, and to decorate carbon nanotubes\textsuperscript{11,12,13} or nano-hornes\textsuperscript{14,15} in artificial photosynthetic devices\textsuperscript{16,17}. Thus, tailor-made porphyrins
Chapter 4 Results and Discussions

and SWNTs complexes might offer, in the future, a valuable technology in the field of nano-optoelectronic devices for energy conversion, sensing and biological applications.\textsuperscript{18,19,20}

In this Chapter, we describe the synthesis of some novel SWNT-porphyrin nanohybrids achieved by both covalent and non-covalent linking strategies. Non-covalent linked SWNTs surface modifications were carried out via supramolecular $\pi-\pi$ stacking of an aryl thioacetate-functionalised hexyl substituted Zn(II)-porphyrin (compound 11). Such porphyrin is a member of a family of substituted porphyrins known to be soluble in most common solvents, e.g. toluene, chloroform, dichloromethane and ethanol. In an alternative procedure, we also applied the Bingel reaction to covalently append this porphyrin, after de-protection, onto the SWNTs outer walls\textsuperscript{21,22,23} based on a thiol-disulphide exchange reliant on the SH-groups of the de-protected Zn(II)-porphyrin (compound 12). For this strategy, the surface of the SWNTs was first modified to contain a thiol group which is capable of reacting with -SH groups of de-protected Zn(II)-porphyrin to generate S-S disulphide bridges\textsuperscript{24}. The newly formed non-covalently linked complex and covalently linked complex were characterised by TEM, SEM and AFM to identify the surface morphology information. Fluorescence and UV-vis analysis were also carried out to investigate the light absorption and emission properties of those complexes. Raman spectroscopy was employed to investigate the complexes’ inner structure. The following equation presents a thiol-disulphide exchange:

$$2\text{RSH} \xrightarrow{\text{Oxidise}} \text{RS-SR} \xrightarrow{\text{Reduce}} \text{RSH}_2$$

Thus, the remaining SWNTs unique electron transport properties combined with the promising porphyrin photo-chemistry mean the complex can work as dispersible solid state materials with applications by means of scaffolds for future
nano-optoelectronic devices. In addition, we also investigated FLIM as a spectroscopic method study of thin film, in which drop-casting a solution of nanohybrids materials onto borosilicate glass, can be used to build up thin film of complexes from the dispersions and then characterise their fluorescence lifetime via single-photon laser confocal fluorescence techniques (FLIM).

4.2. Results and discussions.

4.2.1. Non-covalently linked Zn(II)-porphyrin and SWNTs complex.

For the synthesis of the free-base (compound 10) and Zn(II)-porphyrin (compound 11), the general reaction scheme devised by Twyman and Sanders was significantly modified and adapted to give lab-scale compounds suitable for further functionalisation.\(^\text{25}\) Simply, the method involved 1-iodohexane, pentane-2,4-dione and benzyl 3-oxobutanonate as the starting materials and their synthetic route needed a complete redesign, given that the original methods were not found reproducible.\(^\text{26}\) The hexyl derived pyrrole acted as the basic building unit to build up porphyrins.\(^\text{27,28}\) The side groups of the porphyrin and the metal centre can be further tuned to incorporate several substituents for future photovoltaic application. The Zn(II)-porphyrin has been specifically designed to incorporate four hexyl chains on the side of the macrocyclic ring to get a better solubility in common organic solvents such as CHCl\(_3\). These were found useful at the purification stage as it made the purification and scale-up without reliance on HPLC spectrum alone.
Chapter 4 Results and Discussions

Figure 4.1: Schematic diagram of generation of non-covalently linked Zn(II)-porphyrin@SWNTs complex and the formation a dimer structure (See Appendix D for the information of dimer crystal).

The thioacetate-protected compound 11 was synthesised hereby, and also used in fresh solutions, to avoid deprotection over time and the formation of a disulphide bridge by dithiol porphyrin coupling and resulting in forming side-product (see Figure 4.1). This was necessary as the formation of such dimers in the presence of oxygen and aqueous environments is likely due to occur and affect the π-π porphyrin-SWNTs stacking thus altering the optical properties of the emerging nanocomposite. This also ensures the preservation of a non-covalent monomeric porphyrin unit ready for a controlled donor-acceptor interlayer association with the SWNTs.
Figure 4.1 is the schematic diagram of generation of non-covalently linked compound $11@\text{SWNTs}$ complex. In the non-covalently linked synthesis strategy (with SWNTs as starting materials), a pre-annealing progress was introduced to repair SWNTs surface defects. This pre-annealing step was found to be rather important and it was found to be commonly used in SWNTs non-covalently functionalisation since the repaired intact surface hexagon carbon sp$^2$ structure plays an essential role in supramolecular interactions.

The annealing progress was carried out by heating the de-gassed SWNTs sample up to 1050 °C under a 1:9 mixed ratio hydrogen and under an Argon gas atmosphere. Following the annealing progress, the SWNTs were dispersed in ethanol solution via 30 min sonication and centrifugation to make a fine SWNTs ethanol dispersion. In the meantime, the starting material compound $11$ was dissolved in chloroform (1 mM). The SWNTs ethanol dispersion solution and compound $11$ chloroform solutions were mixed and stirred for 24 hours at room temperature under nitrogen. It is believed that the compound $11@\text{SWNTs}$ complex is likely to be formed via π-π stacking between the pyrrole rings of the centre part of Zn(II)-porphyrin during this time, and the hexagonal rings on the SWNTs surface are involved in this stacking with the porphyrin planes. The final complex materials were washed several times with chloroform and collected by a nano-filtrate system, dried and deemed ready for analysis by spectroscopies and microscopies (see below).

The resulting compound $11@\text{SWNTs}$ complex can form a stable suspension in 1:1 ethanol and chloroform which could be characterised by UV-vis and fluorescence spectroscopy to identify the light absorption and emission behaviour. Raman spectroscopy was used to investigate the inner structure of the non-covalently linked nano-complex. The morphology information of non-covalently linked compound $11@\text{SWNTs}$ complex was analysed by Atomic force microscopy (AFM), Scanning electron microscope (SEM) and Transmission electron microscopy (TEM).
Steady-state fluorescence emission studies involving FLIM were carried out to analyse whether an energy transferred process may occur between SWNTs and the compound 11 in the thin film (obtained by drop-costing this suspension onto borosilicate glass).

4.2.1.1. Solid state investigation by TEM

Figure 4.2: TEM images of non-covalently linked compound 11@SWNTs complex, where (a) the scale bar is 200 nm; (b) the scale bar is 50 nm.

Transmission electron microscopy (TEM) provided the direct visualisation and size information of SWNTs surface area at the level of individual SWNTs and their thin bundles formed. The Figure 4.2 (a) and (b) shows the surface imaging information of non-covalently linked compound 11@SWNTs complex. Figure 4.2 (b) was obtained by use of the same sample as 4.1 (a), but recorded in a magnified area. From TEM images, there were strong contrast areas contributed by heavier elements Zinc (Z = 30) and sulphur (Z = 16) and the compound 11, which were obviously visible compared with the lighter contrast regions (due to the lower scattering elements present, i.e. hydrogen (Z = 1), nitrogen (Z = 7) and carbon (Z = 6) from the SWNTs and porphyrin ligand framework. Figure 4.2 (b) shows more detailed
information that after complexation with compound 11, where the relatively clear and smooth SWNTs surface became irregular in places and there were some aggregations formed on this surface. Perceptibly, the side-wall of SWNT was significantly ‘roughened’ by the coverage of another material, which could be due to the presence of compound 11 that coated the surface of SWNT\textsuperscript{29,30,31,32}. The length of the SWNTs was not altered and the intact SWNTs structure indicated the controlled time sonication (5 min followed by pause, and repeated 3 times) did not introduce significant surface defects observed by this method. The TEM images can also indicate that the SWNTs were better dispersed in ethanol with only a few bundles persisting. More TEM images of non-covalently linked compound 11@SWNTs are presented in Appendix iii, Figure B.1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{supramolecular.png}
\caption{Illustration of supramolecular assembly between porphyrins and single-walled carbon nanotubes in Taku Hasobe’s research\textsuperscript{33}}
\end{figure}

The compound 11 may contribute to the formation some complex bundles. From an analogy with Taku Hasobe’s research\textsuperscript{33}, as shown in Figure 4.3, it can be found that in SWNTs@porphyrin systems, porphyrin molecule can be used as a glue to \(\pi-\pi\) stacking on the surface of SWNTs to combine two functionalised SWNTs together and form an ordered assembly structure. Compared to Taku Hasobe’s research, it was reasonable to assume that the unsuccessful formation of ordered assembly structure in this project was due to the absence of an acidic environment (which could have led to loss of Zn(II) and de-protection) or the enlargement of distance between the two nearby porphyrins caused by the four presence long chains.
and the two side groups on the edge. The Taku Hasobe’s research indicated that the attaching angle of porphyrin and SWNTs was 0 degrees, it means the fact that the combination of porphyrin and SWNTs occurs in a face-face orientation and very small attaching space was needed.

4.2.1.2. Solid state investigation by Field Emission SEM

![SEM image of non-covalently linked compound 11@SWNTs complex, scale bar is 1000nm.](image)

**Figure 4.4:** SEM image of non-covalently linked compound 11@SWNTs complex, scale bar is 1000nm.

SEM measurement of SWNTs and its complex can present more surface information on a larger dimension and with choice indications of the morphology. The SEM measurements were carried out by dropping dispersed complex solution, which were treated with prolonged sonication and centrifugations, onto a HPGO SEM substrate. Due to the conditions and limitations of SEM measurement facilities available, the 200 nm scale bar SEM image was the best magnified scale image that could be obtained. In addition, this SEM instrument machine could not provide the coupled EDX measurement to identify elements simultaneously. Therefore the assignment is only qualitative based on morphology changes with respect to the SWNTs.
Figure 4.5: SEM image of non-covalently linked compound 11@SWNTs complex, scale bar is 200nm.

It can be seen from the SEM images in Figure 4.4 and 4.5, which presented the non-covalently linked compound 11@SWNTs complex surface morphology information, that the coated compound 11 was uniform and covered the entire aromatic surface of SWNTs. After the complexation, there were bumps and aggregations appeared on the SWNTs surface. The functionalised SWNTs were relatively better dispersed than intact SWNTs. The hole size of the network of the compound 11@SWNTs complex was around 200 nm. The zoomed SEM image in Figure 4.5 also gave some evidences, in a related area, to support the hypothesis proposed in TEM section that the porphyrin could contribute to the linking of two or more SWNTs strands together.

4.2.1.3. Solid state investigation by AFM

The AFM spectroscopy measurements of non-covalently linked SWNTs@compound 11 were carried out to further study the surface morphology information of the complexes. Combining TEM, SEM and AFM information, these surface analysis techniques can provide a fuller surface morphology picture and information of the size of this complex nanomaterial.
Figure 4.6: Tapping mode AFM image of non-covalently linked SWNTs@compound 11 complex (Images collected under the supervision of Dr Robert Jacobs, University of Oxford).

Figure 4.7: 3D Tapping mode AFM image of non-covalently linked SWNTs@compound 11 complex (Images collected under the supervision of Dr Robert Jacobs, University of Oxford).

For the non-covalently linked SWNTs@compound 11 complex, AFM measurement was introduced by dropping SWNTs@compound 11 complex dispersion solution (1:1 ethanol and chloroform) onto a HOPG substrate. The use of a Mica substrate was also tested in the sample preparation progress with spin coating, but it
did not give expected result due to the complex being unable to attach on the mica surface well enough for the imaging experiment to succeed. The high quality complex dispersion was prepared though prolonged sonication (30 min) and centrifugations (3500 rpm) which gave a 1 mg/ml stable dispersion over 24 hours without precipitate. The solvent combination for complex dispersion was 1:1 ethanol and chloroform, chosen not only to keep the continuity in disperse phase but also to be easily evaporated after drop-cost onto the HOPG substrate.

The AFM images shown in Figure 4.6 and 4.7 are these corresponding to the non-covalently linked compound 11@SWNTs complex. From those images, the compound 11 is believed to uniformly cover the entire aromatic surface of SWNTs. The surface decorated SWNTs could be relatively better dispersed compared to the raw intact SWNTs. The 3D AFM image shows the sample location and the measure angle, it also indicated the fact that a bundle of functionalised carbon nanotube has a 9 nm height. It is know from TEM information on raw nanotubes that the size of raw (purified but un-functionalised SWNTs) is typically between 1.5-5 nm for Elicarb SNWTs (CVD-synthesised by Thomas Swan).

4.2.1.4. Raman Spectroscopic characterisation

Raman spectroscopy is a powerful bulk-characterisation tool and a widely used technique for investing the vibrational, rotational and other low-frequency modes in carbon nanotubes. It also gives reliable information on the degree of crystallinity of graphitic carbon structure in such materials.34,35 The Raman spectra of non-covalently linked compound 11@SWNTs complex and intact SWNTs were presented in Figure 4.8. They were recorded by dispersing the desired samples in CHCl₃ : EtOH (1:1) and using $\lambda_{\text{ex}} = 830$ nm (At this wavelength, it was found that the fluorescence emission from compound 11 did not interfere with the Raman spectroscopy charactering result).
Figure 4.8: Raman spectroscopy of SWNTs and non-covalently linked compound 11@SWNTs complex.

For intact SWNTs, the G band at 1581 cm\(^{-1}\), this is due to the primary graphitic mode, corresponding to a splitting of the E\(_{2g}\) stretching mode of graphite, reflecting the structural intensity of the sp\(^3\)-hybridized carbon atoms. Also the G band at 1289 cm\(^{-1}\) is present and this is the defect band, which indicates the disordered graphite structure introduced by surface defects of pure SWNTs. The I\(_D\)/I\(_G\) ratio of the intact SWNTs was 0.11 which was a relatively small ratio, indicating there were small amount of impurities or surface defects on the SWNTs used as the starting material.
Figure 4.9: Raman spectroscopy of SWNTs and non-covalently linked compound 11@SWNTs complex.

It can be seen from Figure 4.8 that the Raman spectra of non-covalently linked compound 11@SWNTs complex shows a G band located at 1588 cm\(^{-1}\) and a D band located at 1292 cm\(^{-1}\). A 0.17 I\(_D\)/I\(_G\) band intensity ratio was observed from the Raman spectra of non-covalently linked compound 11@SWNTs complex. Compared with the I\(_D\)/I\(_G\) band intensity ratio with free SWNTs, the ratio of non-covalently linked complex presented an increase of nearly 50%, which indicated the supramolecular self-assembly interaction between SWNTs and compound 11 likely was occurred.

The Raman spectra also show Radial Breathing Mode (RBM) bands which are located between 140 cm\(^{-1}\) and 300 cm\(^{-1}\). From Figure 4.9, the enlarged sections of the Raman spectra of shown in Figure 4.8, shows that the free SWNTs samples contained carbon nanotubes with a broad diameter ranged from 0.8 nm to 1.8 nm, in which there were two significant and sharping RBM peaks at 234 cm\(^{-1}\) and 146 cm\(^{-1}\). These sharp peaks indicate the nanotubes have diameters of 1.02 nm and 1.64 nm based on typical diameter calculations (\(\omega = 239/d\) cm\(^{-1}\)).\(^{36}\) The non-covalently linked compound 11@SWNTs complex also shows two maxima RBM peaks at 240 cm\(^{-1}\) and 154 cm\(^{-1}\),
which indicates that in CHCl₃ : EtOH (1:1) solution, the non-covalently linked compound 11@SWNTs complex dispersions also contain tubes with 0.99 nm and 1.55 nm diameters.

The diameter information reflected by Raman RMB mode corresponded to the radial breath diameter of those tubes. It can be found that after functionalisation and coated with compound 11, the breath ability of carbon nanotube is reduced. Due to the reduced breath ability, it can be reasonably assumed that the compound 11 in the complex was successfully attracting to the tube surface and this extra small molecule reduced the breath ability of the tubes. Only the tubes from the reduced diameters range can be “selected” and “extracted” in the presence of the porphyrin aggregate. This is not surprising, and it shows that the extended, 3D porphyrin aggregate can act as a supramolecular “host” for individual, low diameter SWNTs, asking as guests. Also, a slightly red shift at RBM maxima of compound 11@SWNTs indicated the supramolecular interaction between SWNTs and compound 11 and the formation of non-covalently complex.

4.2.1.5. Two-dimensional fluorescence contour plotting fluorescence imaging characterisation

Two-dimensional fluorescence contour plotting was introduced to investigate the excitation and emission differences between compound 11 on its own and non-covalently interacted with SWNTs. Two-dimensional fluorescence contour plotting measurements of free Zn(II)-porphyrin solution (1:1 ethanol : chloroform, 1µM), SWNTs dispersion (1:1 ethanol : chloroform) and non-covalently linked compound 11@SWNTs complex suspension (1:1 ethanol : chloroform, 1mg/mL) were carried out respectively by exciting from very 10 nm over the 200 nm to 800 nm range and recording emission from 200 nm to 800 nm in 10 nm increments. The fluorescence measurements were normally set to operate overnight, as a result, a lid was needed to cover the sample container to protect from evaporation. The
dispersions used here need to make sure that there were no significant scattering of dispersion occurs during the period of observation.

**Figure 4.10**: Two-dimensional fluorescence contour plotting of (a) compound 11 (in 1:1 ethanol and chloroform, 1 μM); (b) intact SWNTs suspension (in 1:1 ethanol and chloroform).

**Figure 4.11**: Two-dimensional fluorescence contour plotting of non-covalently linked compound 11@SWNTs complex (in 1:1 ethanol and chloroform, 1 mg/mL).

From the two-dimensional fluorescence contour plotting of free compound 11 shown in Figure 4.10 (a), strong emission peaks, in the region from 570 nm to 670 nm were detected. These strong emission regions were due to the highly conjugated π system within compound 11. SWNTs suspension presented no absorption and
emission behaviour according to fluoresce measurement result, strong Rayleigh scattering lines (first and second order) were shown in the two-dimensional contour plotting of SWNTs (Figure 4.10 (b)). In Figure 4.11, the two-dimensional fluorescence contour plotting of non-covalently linked compound 11@SWNTs, the main absorption peak range was significant quench. As well as the disappearance of the emission peak, a blue-shift of maximum emission wavelength from 570 nm - 670 nm to 530 nm - 610 nm can be observed, but the resulting bands have a much lower intensity than in the free compound 11 2D spectrum.

The observation of significant fluorescence quenching behaviour makes it reasonable to assume that in compound 11@SWNTs complex suspension, all free compound 11 molecules were attached onto SWNTs surface via the π-π stacking interaction. The blue-shifts of maximum emission wavelength also exhibited an energy transfer process from compound 11 to SWNTs within the complex system, which confirmed the consequences of the non-covalently adsorption interaction between compound 11 and SWNTs.

4.2.1.6. UV-vis absorption measurements

The UV-vis spectroscopy was introduced to investigate the light absorption behaviour of non-covalently linked complex. Figure 4.12 exhibited the UV-vis optical absorption spectra of intact SWNTs, compound 11 and non-covalently linked compound 11@SWNTs complex. The whole scan range UV-vis spectroscopy of compound 11@SWNTs complex was presented in Appendix F.
Chapter 4 Results and Discussions

Figure 4.12: UV-vis spectra of Zn(II)-porphyrin, SWNTs and non-covalently linked compound 11@SWNTs complex (dispersed in 1:1 ethanol and chloroform solution, 1mg/mL).

From the spectra, it can be found that there were no obvious absorption peak observed in SWNTs UV-vis spectrum, which indicates SWNTs do not absorb in the UV-vis zone. As described in previous chapter, the Zn(II)-porphyrin that applied in nanohybrids synthesis exhibits a main Soret absorption peak at 417 nm and a secondary absorption band at 546 nm. After the interaction with SWNTs, the newly formed compound 11@SWNTs nanohybrids presented an emerging absorption band at 436 nm in the dispersed phase. This emerging absorption band indicated the formation of new nanohybrids via π-π stacking between the conjugated centre of Zn(II)-porphyrin and graphitic sp² carbon atom structure on the surface of single-walled carbon nanotubes. Compared with the intact Zn(II)-porphyrin, in same solvent, and at the similar concentration (1 μM), UV-vis light absorption behaviour of the new nanohybrids exhibits a red shift (from 417 nm to 436 nm) in the main absorption band. This red shifted light absorption behaviour could be reasonably explained by an electron/energy transfer occurring within the Zn(II)-porphyrin-SWNTs donor-accepter system. The emerging and redshifted new
absorption band indicates the formation of new nanohybrids structure, and this is consistent with the literature data for simple porphyrins\textsuperscript{37}.

An assumption had been proposed to further demonstrate both the covalently linking strategy and non-covalently linking strategy could be achieved. A small molecule used as $\pi$-$\pi$ stacking competitive interaction agent with compound 11 was introduced to both complexes systems. Due to the expected high binding constant with compound 11 (the rapid quenching observed), in non-covalently linked strategy, the competitive reaction agent may or may not be able to remove compound 11 from the SWNTs surface. However, it cannot work in a covalently linked system. Coronene was therefore selected as the competitive reaction agent to attempt to remove compound 11 from the surface of SWNTs.

![Absorbance vs Wavelength](image)

**Figure 4.13:** UV-visible absorbance titration of coronene and Zn(II)-porphyrin (compound 11), the insert image is the magnified relevant region, from 405 nm - 430 nm in UV-vis titration spectra. (Magnified relevant region of secondary absorbance band (from 520 nm - 620 nm) can be found in Appendix H)
Figure 4.14: Binding constant of coronene and Zn(II)-porphyrin (compound 11) using a 1:1 binding isotherm (the Y axis is corresponding to the UV-visible absorption change between the compound 11@coronene and intact compound 11 at 422 nm (red line) and 545 nm (blue line); the X axis is the ratio of the concentration of added coronene and such of compound 11).

Recently Dr Zhiyuan Hu observed a non-covalent binding between aromatic electron-poor molecules, such as Naphthalenediimides (NDI) and planar carbon-based materials such as thermally reduced graphene oxide (TRGO), graphene oxide (GO) and coronene. In order to confirm that the π-π interactions between porphyrin and carbon single-walled nanotubes and quantify their supramolecular assembling, host-guest UV-Vis titration was carried out by using coronene, C_{24}H_{12}, (Guest) as model for sp² carbon system and Zn-Porphyrin (Host), where a up- and down-field progressions of the UV-Vis absorbance intensity (Δδ) were recorded. The formation of these HG 1:1 stoichiometries can therefore be described by the following bimolecular equilibrium:

\[ H + G \rightleftharpoons HG \]

The stepwise binding 1:1 constants therefore can be described as:

\[ K_{1:1} = \frac{[HG]}{[H][G]} \]
The mathematical model associated with UV-VIS titrations and used to obtain the binding constant is developed by correlating the [HG] to the change in chemical shift (Δδ) of selected UV-vis absorbance intensity. Δδ can then be described as result of a cumulative contribution of [HG] in the the simplest 1:1 stoichiometries.

\[ \Delta \delta = \delta_{\Delta HG} \left( \frac{[HG]}{[H_0]} \right) \]

In this experiment, a stock solution of Zn-Porphyrin (5 × 10^{-6} M) and Coronene (5 × 10^{-7} M) were prepared in a mixture of chloroform and toluene (1:1). Separately, a solution of Zn-Porphyrin (5 × 10^{-6} M) was prepared in a same mixture solution. Stock solution was gradually added (65 µL) into the cuvette containing Zn-Porphyrin, so that the concentration of Zn-Porphyrin for each UV-Vis experiment was kept constant. The UV-Vis absorption of Porphyrin increased as the equivalents of C_{24}H_{12} were progressively added. These absorption values were collected in a data set (excel files or input files). Then, such data set was analysed by MATLAB m-files and fitted for 1:1, Zn-Phorphyrin:C_{24}H_{12} binding isotherm. This software resulted in $K_a$ and statistic parameters such as statistic error (SE_y) and covariance of fitting (Cov_t). Binding constants and statistic parameters are reported in Table 4.1.

**Table 4.1**: Binding constants and statistic parameters.

<table>
<thead>
<tr>
<th></th>
<th>$K_a$ (M(^{-1}))</th>
<th>$\Delta G^#$ (kJ/mol)</th>
<th>SE(_y)</th>
<th>Cov(_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)-porphyrin</td>
<td>46200</td>
<td>-24.3</td>
<td>0.0038</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

UV-Vis titration data of porphyrin indicated an enhanced absorption peak at 422 nm. There was also a slightly emerging broad peak at 545 nm in non-covalently linked complex filtrate, which corresponded to the secondary absorption band of intact porphyrin. Figure 4.12 presents the UV-visible absorption titration of coronene and Zn(II)-porphyrin, and the insert image is the magnified UV-vis titration spectrum. Plot of experimental $\Delta A$ of Zn(II)-Porphyrrin at $\lambda_{\text{abs}} = 545$ nm (blue markers), $\lambda_{\text{abs}} =$
422 nm (red markers), fitting curves (blue and red solid lines for 1:1) and fitting models are also reported in Figure 4.14. The resulting $K_a (46200 \text{ M}^{-1})$ is a relatively high binding constant and it means that coronene was therefore selected as the competitive reaction agent to attempt to remove compound 11 from the surface of SWNTs.

**Figure 4.15:** UV-vis spectra of compound 11, SWNTs and non-covalently linked compound 11@SWNTs complex after adding with coronene and washing, dispersed in 1:1 ethanol and chloroform solution.

As discussed above, to further investigate $\pi-\pi$ stacking interaction between compound 11 and SWNTs and identify the linkage difference between non-covalently linked complex and covalently linked complex, coronene was introduced as a competitive reagent in SWNTs and compound 11 systems. Due to the strongly delocalised electron density, coronene can form strong interactions with porphyrin molecule compared with SWNTs. Coronene was added into the non-covalently linked compound 11@SWNTs suspension and then the mixture was washed by toluene several times. The final products were collected by a filtration system. Both filtrate and solid were collected. After adding coronene and completing washing process, the final products were re-dispersed in 1:1 ethanol and chloroform solution, Figure 4.15 shows the UV-vis measurement results for intact compound 11@SWNTs, SWNTs, and SWNTs after treatment with coronene and a toluene wash.
to remove any unboned coronene. It can be observed from the measurement that the previous absorption band at 436 nm for non-covalently linked compound 11@SWNTs complex disappeared and the final products exhibited a similar UV-vis absorption spectra as the intact SWNTs, which indicated that after adding coronene and the toluene wash, the Zn(II)-porphyrin was successfully pulled off from the surface of SWNTs, and likely formed a new compound 11@coronene complex.

![Figure 4.16: UV-vis spectra of Zn(II)-porphyrin, coronene and the filtrate of non-covalently linked compound 11@SWNTs complex after adding with coronene and washing, dispersed in 1:1 ethanol and chloroform solution.](image)

Figure 4.16 shows the UV-vis measurement of filtrate of non-covalently linked complex after addition with coronene and several times toluene wash. Compared with the results of intact compound 11, coronene and filtrate solution, it can be found that in the filtrate solution, the absorption band at 420 nm was enhanced and the absorption band at 450 nm disappeared, there was also a broader peak which emerged at 546 nm, which corresponded to the secondary absorption band of intact compound 11. All those enhanced peak and disappearing peaks indicated that in the filtrate solution, the coronene and compound 11 were linked together to form a new complex structure. The new formed structure was then confirmed by previous assumption that in non-covalently linked compound 11@SWNTs, the compound 11 can be removed
from the surface of SWNTs by adding coronene into the system to give compound 11@coronene instead.

4.2.1.7. UV-vis titration between SWNTs and Zn(II)-porphyrin

\[ \text{Absorbance (a.u)} \]

\[ \text{Wavelength (nm)} \]

\[ 400 \quad 450 \quad 500 \quad 550 \quad 600 \]

\[ 0.00 \quad 0.05 \quad 0.10 \quad 0.15 \quad 0.20 \quad 0.25 \quad 0.30 \quad 0.35 \]

Addition of SWNTs

\[ 0 \quad 1000 \quad 2000 \quad 3000 \quad 4000 \]

\[ \text{Added volume of compound 11@SWNTs complex (μL)} \]

\[ 0 \quad 0.05 \quad 0.1 \quad 0.15 \quad 0.2 \quad 0.25 \quad 0.3 \]

(b)

**Figure 4.17:** (a) UV-visible absorbance enhance behavior of non-covalently linked compound 11@SWNT complex; (b) UV-visible absorbance intensity with respect to added volume (430 nm).

The superamolecular assembly of compound 11 and SWNTs may be regarded as the non-covalently linked complex and has been studied by using optical
spectroscopy in a mixture of organic solvents which is suitable to disperse all components. The Figure 4.17 shows the UV-visible optical absorption spectra of Zn(II)-porphyrin dispersed in 1:1 o-DCB and chloroform (3mL, 1 μM) then titrated with Zn(II)-porphyrin (0.5 μM) and SWNTs dispersed in the same 1:1 o-DCB and chloroform solution (around 1 mg/mL). For titration measurement of SWNTs and compound 11, the quality of SWNTs dispersed solution plays an essential role. The solvent combination, ethanol and chloroform, was chosen due to their solubility and ability to generate stable dispersion with respect to precipitant over 24 hour. Ethanol was used to disperse SWNTs and chloroform was used to dissolve compound 11.

As shown in Figure 4.17, the addition of SWNTs into compound 11 solution resulted in an enhanced intensity of the optical absorption and the Soret band of free compound 11 which located at 417 nm was then a slightly red shifted to 430 nm. This red shifted peak and spectroscopic overall collectively suggest that upon the addition of SWNTs into compound 11 solution, an electron donor-acceptor interaction system was formed due to the π-π stacking interaction between free compound 11 and SWNTs. During the self-assembly progress, the Soret band of intact free compound 11 (417 nm) disappeared likely because all porphyrin molecule were attached onto the surface of SWNTs. The newly formed, non-covalently linked compound 11@SWNTs complex presented an emerging absorption peak at 430 nm, and this peak seems enhanced when the concentration of the new formed complex was increased as expected in the absence of aggregation. The observed 430 nm peak in the titration progress was also corresponded with the UV-Visible absorption measurements of non-covalently linked compound 11@SWNTs shown in figure 4.12. The UV-visible titration measurements of compound 11 and SWNTs, especially the red shifted Soret band and enhancement of new band intensity, provided direct evidence of some energy transfer occurring between SWNTs and compound 11.
4.2.1.8. Confocal fluorescence microscopy imaging

In order to further study the interaction and energy transfer between SWNTs and Zn(II)-porphyrin, single-photon laser confocal fluorescence measurement was introduced to characterise fluorescence lifetime. The figure 4.18 shows lifetime emission maps of solid-state non-covalently linked compound 11@SWNT complex was measured under $\lambda_{ex}=473$ nm. The single-photon intensity maps showed the spatial variations in fluorescence emission. The lifetime imaging maps (Figure 4.19) presents corresponding distribution curve together and shows the predominant lifetime component ($\tau_1$) for compound 11@SWNT complex. It can be seen from the corresponding lifetime distribution curve that the major lifetime measured in compound 11@SWNT complex was $2000\pm 100$ ps. A relatively broader FWHM (full width at half of the maximum) of the corresponding lifetime distribution curve, which is nearly 400 ps, was observed. This broader FWHM suggest the low homogeneity of fluorescence lifetime decay and also points towards the formation of the hybrids structure for the thin film studies.

![Figure 4.18: Single-photon laser confocal fluorescence: (a) solid-phase non-covalently linked Compound 11@SWNTs complex, intensity image, the measured area is 30 μm × 30 μm; (b) lifetime and correspond mapping and scale bar in ps.](image)
4.2.1.9. Summery to non-covalently linked complex compound 11@SWNTs formation

In this sub-section, a novel non-covalently functionalised complex formed between SWNTs and the compound 11 was synthesised by a novel method, which has been proposed and demonstrated hereby. In this interaction, the Zn(II)-porphyrins are likely to be attached onto the surface of SWNTs via aromatic ring stacking, which seems less strong respect to the covalently-SWNTs interactions. The morphology of non-covalently linked compound 11@SWNT complex was investigated by TEM, SEM and AFM. From the TEM images, it can be found that after the interaction with compound 11, the nano-dimensional surface of SWNTs appeared uneven and there were also some aggregations formed, likely due to porphyrin stacking. SEM measurements offered information on the surface morphology on μM scale. From the SEM images it emerged that the compound 11 coated entirely the surface of the SWNTs and, after the supramolecular modification with compound 11, the SWNTs are arranged as a network-like structure. The AFM measurement was carried out to obtain the nanomaterials height information and to try and assess the ability of individual strands to disperse in the organic solvent. This gave surface information at
higher magnification. AFM images showed that the compound 11@SWNT remained in a single strand 1-dimensional structure and the height of the complex was around 9 nm, whilst the length of starting intact SWNTs was around 1-5 nm. The inner structure of the complex was studied by Raman spectroscopy. The fluorescence emission behaviour of compound 11@SWNTs was carried out by two-dimensional fluorescence contour plotting measurements. The spectra showed that the addition of SWNTs causes a blue shifted main emission band and also a strong fluorescence quenching behaviour, which means that all free compound 11 molecule were attached to the SWNTs surface. The UV-vis measurement of the non-covalently linked compound 11@SWNT complex exhibits a main absorption band at 436 nm. In order to further identify the non-covalently linked reaction, coronene was introduced as a competitive reacting agent, which driving to probe the coronene@SWNTs formation is preferential. From the UV-vis measurement, it was confirmed that the coronene molecule can successfully remove the compound 11 off from the SWNTs surface. UV-vis titration measurement of compound 11 and SWNTs showed that after the addition of SWNTs, the main absorption peak of free compound 11, at 417 nm, disappeared and there was a new absorption peak emerged at 430 nm. This suggests the formation of the non-covalently linked complex compound 11@SWNTs in solution. The single-photon laser confocal fluorescence measurements in the thin film were also confirmed the formation of the new complex system by giving a new main fluorescence lifetime range with a wide FWHM.

In a summary, the formation of a novel compound 11@SWNTs complex was demonstrated and the surface morphology, inner structure and light absorption/emission properties of this complex were fully investigated. This material retains some of the UV-Vis, fluorescence and Raman characteristics of the free compound 11.
4.2.2. Covalently linked Zn(II)-porphyrin and SWNTs complex.

The synthesis strategy for a new-covalently linked SWNTs@Zn(II)-porphyrin complex was introduced and compared with the non-covalently linked strategy for the complexes discussed above. The covalently linked compound 11@SWNT was carried out by introducing the Bingel reaction to covalently modify the outer SWNTs walls by the SH- de-protected Zn(II)-porphyrin. For this strategy, the surface of the SWNTs was firstly modified to a thiol group, which is then capable to react with -SH groups of de-protected Zn(II)-porphyrin and generate S-S disulphide bridges (See Figure 4.20).

![Diagram of generation of the covalently linked compound 11@SWNT complex.](image)

**Figure 4.20:** Schematic diagram of generation of the covalently linked compound 11@SWNT complex. For clarity, only one porphyrin is shown hereby. (For the formation of the dimer side products structure, see Appendix D for X-ray information).
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As is presented in Figure 4.20, the Bingel reaction chosen here to functionalisation takes place via the interaction of SWNTs with diethyl bromomalonate and 1,8-diazabicyclo[5.4.0]undecene. Next, the ethoxy groups introduced were then further converted to thiol groups by treatment with 2-mercaptoethanol. The functionalised SWNTs were then dispersed in ethanol by a prolonged time sonication and centrifugation step (15 min, 3500rpm). The de-protected reaction for compound 11 was carried out immediately before the covalently linked strategy was applied. This was important as is needed to balance the presence of the de-protected compound 11 in fresh solutions to avoid the formation of a disulphide bridge by dithiol porphyrin coupling. This was necessary, as the formation of such dimers and oligomer due to the prolonged exposure to oxygen and aqueous environments, it is known that this process will block the thiol group and in addition, the dimer could also lead to the π-π stacking between dimeric porphyrin and SWNTs, thus altering the optical properties of the emerging nanocomposite. As such ensuring the preservation of a non-covalent monomeric porphyrin unit that was ready for a controlled donor-acceptor interlayer association with the SWNTs was a force driving this synthesis. Thioacetate-protected compound 11 was reacted with hydrazine monohydrate in degassed CH₂Cl₂ overnight aiming to covert the protection acetate groups to thiol groups. The S-S disulphide bridges formation was then used as the linkage of choice to combine functionalised SWNTs and de-protected compound 11. The starting materials were stirred together for 72 hours in the presence of DBU and under air. The final covalently linked complex products were then purified several times by washing and with organic solvents, which should remove all non-bonded porphyrins, and collected by a nano-filtration system. From this filtrate, crystal of the dimer could be isolated and X-ray measurements confirmed that the structure is the same with that of the known dimer. (See Appendix D)

The final covalently linked complexes were then characterised by TEM, SEM and AFM to identify the complex surface morphology information. The light
absorption and emission properties were characterised by UV-vis and fluorescence measurement. Raman spectroscopy was introduced to indicate the inner structure of the covalently linked SWNTs@Zn(II)-porphyrin complex. In addition, we also investigated a complex thin film, which was generated by drop-casting a solution of the complex onto borosilicate glass, and recording their fluorescence lifetime via single-photon laser confocal fluorescence.

4.2.2.1. Solid state investigation by TEM

TEM measurements were carried out to obtain the surface morphology information of covalently linked SWNTs@compound 11 complex. Samples were obtained by drop-costing the nano-complex materials, from an ethanol dispersion onto a lacy carbon TEM grid. Figure 4.21 shows the measurement results with two different magnifications (200 nm and 50 nm scale bar respectively).
Figure 4.21: TEM image of (a) covalently linked compound 11@ SWNTs complex, the scale bar is 200 nm; (b) covalently linked compound 11@ SWNTs complex, the scale bar is 50 nm; (c) Energy-dispersive X-ray spectroscopy (EDX) analysis of SWNTs@compound 11

From the TEM images, it can be seen that the contract was due to different molecular weight of the components, as the Zn and S gave darker part, while the lighter region contributed by the presence of carbon or nitrogen. The TEM images also indicated that after functionalisation by Bingel and further modifications, the SWNTs still retain tubular structures and that the lengths of SWNTs were not altered. After the covalently linked with compound 11, the surface of SWNTs can be found
clearly altered and some aggregations were also visible on the surface. It is reasonable to assume that those dark points appeared on the surface of SWNTs were the reaction sites where the compound 11 was grafted onto with SWNTs strands. EDX measurement also proofed the Zn element presence. Additional TEM images of the covalently linked compound 11@SWNTs are presented in Appendix iv, Figure B.2.

4.2.2.2. Solid state investigation by Field Emission SEM

The Field Emission SEM measurements of compound 11@SWNTs were carried out to explore more surface morphology information over μm scale area of investigation. The SEM measurements were carried out on samples generated by drop-casting a dispersion of the covalently linked complex solution (which was treated with a prolonged time sonication (15 min) and centrifugation (15 min, 3500 rpm)) onto a HPGO substrate.

![SEM image of covalently linked compound 11@SWNTs complex, scale bar is 1000 nm.](image)

**Figure 4.22:** SEM image of covalently linked compound 11@SWNTs complex, scale bar is 1000 nm.
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Figure 4.23: Magnified SEM image of covalently linked compound 11@SWNTs complex, scale bar is 500 nm.

The SEM images shown in Figures 4.22 and 4.23 were the results obtained in the covalently linked complex: it can be seen from the SEM images that the Zn(II)-porphyrin, linked covalently, uniformly covered the entire aromatic surface of SWNTs. After the complexation with Zn(II)-porphyrin, SWNTs surface become very uneven and strands were found bundled together. Compared with the images of intact CVD-synthesised SWNTs, the covalently functionalised SWNTs exhibited enhanced dispersion properties under similar measurement conditions. Compared to the non-covalently functionalised compound 11@SWNTs complex, the analogous covalently functionalised complex exhibited a different surface morphology. The covalently linked complex presented a porous structure, which is similar to non-covalently linked complex, but the size of the aggregates was much smaller (200 nm vs 50 nm, respectively).
4.2.2.3. **Solid state investigations by AFM**

The AFM measurements were applied in this project to further study the surface morphology information of covalently linked, de-protected compound 11 attached onto the SWNTs. The AFM measurements were carried out via dropping complex suspension onto a HOPG substrate. In AFM sample preparation and characterisation process with respect to SWNTs, because of the different electron charges and hydrophilic properties, a mica substrate measurement which was also attempted but failed to generate interpretable data.

![Tapping Mode AFM image of covalently linked compound 11@SWNTs complex.](image)

**Figure 4.24:** Tapping Mode AFM image of covalently linked compound 11@SWNTs complex.
Figure 4.25: 3-Dimensional Tapping Mode AFM image of covalently linked
de-protected compound 11 linked onto SWNTs.

Figure 4.24 presents the results obtained for the covalently linked complex,
compared with the intact SWNTs AFM images. It can be found that after the surface
modification and functionalisation with compound 11, the SWNTs could be better
dispersed in common solvents (1:1 ethanol and chloroform). The 3-D tapping mode
AFM image (Figure 4.25) exhibited an 11 nm height and showed that the SWNTs
surface became uneven, stacks of the de-protected compound 11 molecules coated the
entire surface of SWNTs.
4.2.2.4. Spectroscopic characterization by Raman

![Graph showing Raman spectroscopy results](image)

**Figure 4.26:** Raman spectroscopy of SWNTs, Bingel reaction functionalised SWNTs and covalently linked compound 11@SWNTs complex.

The spectra presented in Figure 4.26 are the Raman spectra of the recorded intact SWNTs, Bingel reaction functionalised SWNTs and covalently linked compound 11@SWNTs complex. Those Raman spectra were recorded by excitation at 830 nm.

**Table 4.2:** Table of ID/IG band intensity of different types of single-walled carbon nanotubes and their complexes.

<table>
<thead>
<tr>
<th>The type of single-walled nanotube or their complex</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified single-walled nanotubes (starting material)</td>
<td>0.11</td>
</tr>
<tr>
<td>Non-covalently linked compound 11@SWNTs complex</td>
<td>0.17</td>
</tr>
<tr>
<td>Bingel reaction functionalised SWNTs</td>
<td>0.16</td>
</tr>
<tr>
<td>Covalently linked compound 11@SWNTs complex</td>
<td>0.19</td>
</tr>
</tbody>
</table>
The intact SWNTs Raman spectra presents the G band at 1581 cm\(^{-1}\) (primary graphitic mode) and G band at 1289 cm\(^{-1}\) (defect band). Whereas the Raman spectra of Bingel reaction functionalised SWNTs exhibits a G band at 1585 cm\(^{-1}\) and a D band at 1289 cm\(^{-1}\). It is commonly known that \(I_D/I_G\) band intensity ratio reflects the degree of crystallinity of graphitic carbon structure in carbon nanotubes. It can be seen that the \(I_D/I_G\) band intensity ratio of Bingel reaction functionalised SWNTs (\(I_D/I_G = 0.16\)) has been dramatically increased compared to the \(I_D/I_G\) band intensity ratio of the free SWNTs (\(I_D/I_G = 0.11\)), which indicated that Bingel reaction introduced a significant of surface defects and disordered graphite structures onto the surface of SWNTs stands materials used.

Compared to the non-covalently linked compound 11@SWNTs complex, the Raman spectra of covalently linked complex of the de-protected porphyrin 11 exhibited a G band locates at 1588 cm\(^{-1}\) and a D band locates at 1293 cm\(^{-1}\) and a slightly increased \(I_D/I_G\) band intensity ratio of 19%. Comparing the \(I_D/I_G\) band intensity ratio of intact free SWNTs with the ratio found for either the non-covalently linked complex (0.17) or the covalently linked complex (0.19), it can be found that both the supramolecular fictionalisation and the covalently modification have occurred.

The Radial breathing modes (RBM) (Figure 4.27) exhibit more details about the radial expansion-contraction of the free intact SWNTs, Bingel-reaction functionalised SWNTs (CVD-prepared and purified) and the covalently linked de-protected compound 11@SWNTs.
Figure 4.27: Raman spectroscopy of SWNTs, Bingel reaction functionalised SWNTs and covalently linked compound 11@SWNTs complex.

The free SWNTs sample used as the starting material contains tubes with a broad diameter range (from 0.8 nm to 1.8 nm), as there are two significant and sharp RBM peaks at 234 cm\(^{-1}\) and 146 cm\(^{-1}\). The spectrum of SWNTs functionalised by the Bingel reaction remained almost unchanged with respect to that of the free SWNTs, which exhibited two maxima for the RMB bands at 234 cm\(^{-1}\) and 145 cm\(^{-1}\), pointing to the tubes with calculated diameters of 1.02 nm and 1.64 nm. Compared to the intact free SWNTs, the maxima RBM peaks of covalently linked, de-protected compound 11@SWNTs complex presented red shifted peaks at 240 cm\(^{-1}\) and 152 cm\(^{-1}\). Those RBM peaks indicate the presence of tubes with calculated diameters of 0.99 nm and 1.57 nm. The diameter information reflected by the Raman RMB mode corresponded to the radial breaking diameter of carbon nanotubes. It could be found that after the modification by the Bingel reaction, the diameter of the resulting modified SWNTs did not present significant changes compared with the case of the free intact SWNTs. Taking the Bingel reaction \(I_D/I_G\) band intensity ratio into consideration alone, it can be reasonably claimed that although the Bingel reaction introduces a cyclopropane structure onto the surface of SWNTs, this disorder defects did not affect the tubes breath ability too much, and RBM remain largely unmodified.
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As stated, the calculated diameter information reflected by Raman RBM mode was corresponded to the radial breath diameter of those tubes. It can be found that after the covalently linking with the Zn(II)-porphyrin, the breath ability of the functionalised carbon nanotube was reduced. This could allow the reasonable assumption that the Zn(II)-porphyrin in the complex system was successfully attached on the tube surface, which reduced the breath ability of the tubes. Thus, this decreasing calculated diameter covalently linked compound 11@SWNTs complex indicated that there were some new interactions occurring within the SWNTs due to the close connection of the attached Zn(II)-porphyrin, and also the formation of a covalently linked SWNTs@Zn(II)-porphyrin complex. Comparing the non-covalently and covalently linked strategies, both complexes showed red shifts in the RBM bands, and the calculated diameters for both complexes are similar.

4.2.2.5. Two-dimensional fluorescence contour plotting and fluorescence imaging characterisation

Two-dimensional fluorescence contour plotting measurements were carried out among the Zn(II)-porphyrin, intact SWNTs and compound 11@SWNTs to identify their fluorescence emission behaviours and the emission differences between non-covalently linked and covalently linked compound 11@SWNTs complex.

\[\text{Figure 4.28: Two-dimensional fluorescence contour plotting of (a) Zn(II)-porphyrin; (b) intact SWNTs suspension.}\]
Figure 4.29: Two-dimensional fluorescence contour plotting of covalently linked compound 11@SWNTs complex (1:1 Chloroform and ethanol, 1 mg/mL).

As above, the 2-dimensional fluorescence contour plotting measurements of free Zn(II)-porphyrin were carried out under 1:1 ethanol : chloroform solution; the intact SWNTs and de-protection compound 11@SWNTs suspension were recorded in 1:1 ethanol : chloroform mixture. The measurements were carried out by excitation from 200 nm to 800 nm and recorded emission form 200 nm to 800 nm respectively. It can be seen found that the intact Zn(II)-porphyrin (in Figure 4.26 (a)) shows a strong emission peak emerging from 570 nm to 670 nm due to the energy transferred between the exited state and ground state. SWNTs suspension still presented no absorption and emission behaviour (Figure 4.28 b), and only two strong Rayleigh scattering (first and second order) lines were observed in the resulting map.

From Figure 4.29, the two-dimensional fluorescence contour plotting of the covalently linked compound 11@SWNTs complex exhibited a weak emission band in the main emission region of the map, compared to the intact Zn(II)-porphyrin, which expanded between 570 nm to 670 nm. The main emission regions for compound 11@SWNTs complex were red shifted from 520 nm to 590 nm. Compared with non-covalently linked and covalently linked compound 11@SWNTs complexes, similar fluorescence quenching behaviours were observed, but the quenching behaviours for covalently linked compound 11@SWNTs complex seems more intense.
The red shift emission and fluorescence quenching behaviour indicated that after the interaction with SWNTs, the free compound \( \text{11} \) were almost all attached on the surface of SWNTs. The red-shifts also exhibited an energy transfer process occurred between compound \( \text{11} \) and SWNTs during the complex system, which could be considered a consequence of the generation of covalently linked complex structure.

4.2.2.6. UV-vis spectroscopy measurement

For the measurement of UV-vis spectroscopy carried out for the SWNTs, intact compound \( \text{11} \) and covalently linked compound \( \text{11@SWNTs} \) complex spectra were shown in Figure 4.30. It can be seen from these spectra that the SWNTs dispersion did not present any obvious absorption band while the compound \( \text{11} \) exhibited a strong Soret absorption peak at 417 nm and also a secondary absorption band at 546 nm. It can also show a bond at 315 nm, characteristic to the SWNTs present in dispersion phase. (See the whole scan range UV-vis spectroscopy of covalently linked compound \( \text{11@SWNTs} \) complex was presented in Appendix F.)

![Figure 4.30: UV-vis spectra of Zn(II)-porphyrin (1 μM), SWNTs and covalently linked compound \( \text{11@SWNTs} \) complex (1:1 ethanol and chloroform solution, 1mg/mL).](image-url)
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For the covalently linked de-protected compound $11@$SWNTs complex, spectrum exhibited a main absorption band at 420 nm. This main absorption band was red shifted compared to that found in the spectrum of free compound $11$ (Condition: $1\mu$M, 1:1 ethanol and chloroform solution). A similar red-shifting behaviour for Soret band been observed in the case of the non-covalently linked compound $11@$SWNTs complex, these non-covalently linked complex presents an absorption band at 436 nm under similar conditions. The difference between the red shift of the characteristic bands of those complexes in the studied system may due to the different linkage methodology. This red shift light of the absorption of the covalently linked compound $11@$SWNTs system indicated the formation of a new complex system. Compared to the case of the non-covalently linked complex, the different measurement results also confirmed the covalently linking strategy was successful.

Similar with the case discussed for non-covalently linked complex (section 4.2.1.6), coronene was introduced into the compound $11@$SWNTs dispersion to probe connectivity, due to its high binding constant with compound $11$ ($46200 \text{ M}^{-1}$). It has also been demonstrated earlier that the coronene can remove compound $11$ off from SWNTs surface in the non-covalently linked complex system. However, in the covalently linked system, the compound $11$ were strongly linked onto the surface of SWNTs by a disulphide bridge, which could mean that unlike the case of the non-covalently linked complex, the coronene molecule should not be able to remove the covalently linked Zn(II)-porphyrin off from the system. After the coronene has been washed out, the complex system remained the same electronic properties compared with previous dispersed solution.
**Figure 4.31:** UV-vis spectra of compound 11 (1 μM, 1:1 chloroform and ethanol), SWNTs and covalently linked compound 11@SWNTs complex after adding coronene and washing.

**Figure 4.32:** UV-vis spectra of Zn(II)-porphyrin (1 μM, 1:1 chloroform and ethanol), coronene and the filtrate of covalently linked SWNTs@Zn(II)-porphyrin complex after washing.
In the competitive reactions set-up, firstly, coronene was added into the covalently linked compound 11@SWNTs complex dispersion, the mixture was stirred overnight, to allow for the starting materials to fully interact with each other. Secondly, the complex was then washed several times with toluene to make sure there were no free (unband) coronene molecules or free porphyrin left. Afterwards, both the complex solid and filtrate phases were collected by a nano-filtrate system and analysed.

UV-vis absorption measurements were carried out in both complex dispersion and resulting filtrate. Figure 4.31 presented the UV-vis absorption results for compound 11, intact SWNTs and covalently linked complex after addition of coronene and washing. It can be found from the resulting spectra, that the compound 11@SWNTs complex still exhibited a main absorption peak at 420 nm, which corresponds to covalently linked complex without introducing coronene (as presented in Figure 4. 30). Comparing this result with the case of the non-covalently linked complex, whereby the experiment was also carried out with similar conditions at the coronene addition and washing process, the remaining peak clearly indicated the covalently linked strategy was successful.

Figure 4.32 shows the UV-vis absorption of compound 11, intact coronene and the filtrate solution. It can be found that for the covalent linking strategy, the filtrate phase exhibits same UV-vis absorption spectra compared with the spectrum of the intact coronene molecule. This result, unlike the case of the non-covalently linked complex, did not present any absorption peak from the compound 11. This means that the filtrate solution contained only the coronene molecule and that no free compound 11 could be removed from the SWNTs by this method. Together with Figure 4.31, it can be confirmed that the de-protected compound 11 was covalently attached onto the surface of SWNTs.
4.2.2.7. Confocal fluorescence microscopy

Similar photon confocal fluorescence microscopy coupled with FLIM were carried out under $\lambda_{ex}=473$ nm in thin film phase. Figure 4.33 and 4.34 shows the lifetime emission maps recorded in the solid-state for the covalently linked de-protected compound 11@SWNTs complex by using same condition as the measurement carried out for non-covalently linked complex (which was shown in Figures 4.18 and 4.19). From the corresponding lifetime distribution curve, the covalently linked compound 11@SWNTs complex presented an average lifetime of 1400±100 ps. A relatively broad FWHM (full width at half of the maximum) of the corresponding lifetime distribution curve (nearly 500 ps) was also observed, comparing with the case of the non-covalently linked complex discussed. This broader FWHM indicated a lower homogeneity of fluorescence decay and points towards the formation of a nanohybrid structure. The difference in the major lifetime components from covalently complex and non-covalently complex also addressed the fact that the formation of those two types of complexes was successful.

![Figure 4.33: Single-photon laser confocal fluorescence: (a) solid covalently de-protected compound 11@SWNTs complex, intensity image; the measured area is 30 μm × 30 μm (b) lifetime mapping and scale bar.](image)
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4.2.2.8. Conclusion to covalently linked Zn(II)-porphyrin@SWNTs

The synthesis of a newly designed covalently linked de-protected compound 11@SWNTs complex was investigated. In this synthesis, the SWNTs were initially functionalised by the Bingel reaction and then further converted by incorporating in the attached groups, two unprotected thiol groups. The de-protected compound 11 was next covalently linked to the functionalised SWNTs by disulphide bridge formation. Similar to the case of the non-covalently linked complexes, structural characterisations were carried out on the covalently linked complex, and the surface morphology information of covalently functionalised complex were obtained by TEM, SEM and AFM. From the TEM images, it can be seen that after the incorporation of

Figure 4.34: Corresponding lifetime distribution curve.

The cyclic voltammetry characterisations for both non-covalently and covalently linked compound 11@SWNTs complex were also carried out. However, it might due to the compound 11 was not present in high enough concentrations for a observed oxidation/reduction current or the working dispersion was not ideal, the cyclic voltammetry result did not indicate any difference between those two strategies. Cyclic voltammetry data of non-covalently and covalently linked compound 11@SWNTs complex were presented in Appendix xiv, Figure E.1 to figure E.3.
compound 11, the SWNTs surface became uneven and there were some aggregations formed on the surface of SWNTs strands. SEM measurements also confirmed the compound 11 covered the entire SWNTs surface. The inner structure of compound 11@SWNTs was investigated by Raman spectroscopy. From the Raman measurements, a modification in the $I_D/I_G$ ratio indicated the fact that after the functionalisation by Bingel reaction, and linking with compound 11, the degree of graphitic crystallinity in SWNTs was decreased. Two-dimensional fluorescence contour plotting measurements were carried out to identify the light emission behaviour of the covalently linked complex. Intense fluorescence quenching behaviour has been found compared with non-covalently linked complex. Coronene was also introduced as a competitive reaction candidate into the covalently linked system. Since the covalently linked chemical bond was formed, the coronene cannot pull the compound 11 off from the SWNTs. This result confirmed by the UV-vis measurements that the complex still exhibited a main absorption band at 420 nm even after adding coronene, follow by filtrate and washing. The measured result of single-photon laser confocal fluorescence also confirmed the formation of the novel covalently linked complex system by showing a different average fluorescence lifetime 1400 ps compared with non-covalently linked complex 2050 ps and a wide (500 ps vs 400 ps) FWHM. Overall, the formation of a novel covalently linked complex was demonstrated and the complex surface morphology, inner structure and light absorbance and emission properties were fully investigated in the dispersed phase and in the thin film.
4.3. References to Chapter 4

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*Physical Chemistry B*, 2003, **107**, 10453-10457.


Chapter 5 Interactions Between an Aryl Thioacetate-Functionalised Zn(II)-Porphyrin and Graphene Oxide/Reduced Graphene Oxide

5.1. Overview

Graphene has rapidly become one of the most popular materials since it was discovered by Geim et al using a simple Scotch tape method.\(^1\) The atomically thin 2D structure, which consists of sp\(^2\)-hybridised carbons, generate remarkable electronic and mechanical properties.\(^2\) These properties make graphene take up a leading position as the next-generation material in the applications of nanoelectronic devices, such as future photovoltaics, transparent conductive films, electrical energy storages and biosensors.\(^6\)\textsuperscript{-10}\) Generally, there are three methods to synthesise graphene so far: (1) the mechanical exfoliation, (2) the chemical vapour deposition (CVD) and (3) the chemical or thermal reduction of graphene oxides. Due to the low cost and less requirements for production equipment, chemical reduction of graphene oxide seems the most simple way to generate graphene, which has a reasonable yield to meet the demand of further sustainable chemistry applications.\(^11\) However, the chemical reduction method cannot fully reduce graphene oxide and there remains an amount of oxygen containing groups attached onto the sheet surface.\(^12,13\)

Graphene oxide (GO), as discussed in Chapter 2 is widely available as a bulk material ready for chemical derivatisation. As such, this layered material can be obtained by the controlled oxidation of graphite has also been studied according to the context of sustainable chemistry applications. Despite a disordered atom arrangement compared with pure graphene, GO retains the nanometre “2D” dimension and offers the advantages of facile chemical manipulations. The electronic and mechanical properties of graphene oxides are considerably inferior to the pure graphene, but since it is more amenable to
chemical derivatisation and is able to be bulk produced under sustainable conditions, this material still presents promising applications towards transparent conductive material and hybrids formation. The existence of numerous oxygen containing groups, such as -COOH, -OH and -O- functionalities at the basal planes of GO sheets renders this material amenable to form stable aqueous dispersions. The spectroscopic characteristics of graphene oxides are tuneable by adjusting the percentage of oxygen groups and the number of carbon atom layers per film. The fluorescence measurements demonstrated the fact that after complexation with some small molecules, GO can exhibit fluorescence behaviour.\textsuperscript{14} It has also been demonstrated that there are potential applications for employing graphene oxide into the photovoltaics generation. Recently, studies found that GO can be functionalised with small molecules: for instance GO was found to be strongly bonded with p-phenylene diamine, which can be used as a dispersing agent for GO in organic solvents.\textsuperscript{15}

Porphyrrins, as a planar, electron-rich and aromatic material have been demonstrated to show a remarkably high extinction coefficient in the visible region. Porphyrrins have already been used in some recent studies involving carbon nanomaterials as the chromophores, as they have the ability to act as dispersing agents and to decorate carbon nanotubes\textsuperscript{16} and nanohornes\textsuperscript{17} to form nanohybrids. This novel nanohybrid material can be used in the development of artificial photosynthetic devices and may be of relevance to PV constructions.\textsuperscript{18}

In this project, a novel porphyrin-based nanohybrid was synthesised whereby the surface modification of graphene oxide was carried out via supramolecular functionalisation using an aryl thioacetate-functionalised hexyl substituted Zn(II)-porphyrin (compound \textit{II}), discussed in the previous chapter. This is a rather unexplored member of a family of substituted porphyrrins known to be soluble in most common solvents e.g. toluene, dichloromethane, ethanol. This is of interest as uniform dispersions of such graphene oxide composite or nanohybrids may be used as a thin layered material with the applications as scaffolds for future nano-optoelectronic devices.
In additional, a novel method to build up a solid state 3-Dimensional reduced graphene oxide and porphyrin composite was also investigated as an approach to optoelectronic devices assembly.

5.2. Results and discussions.

5.2.1. Assembly of two-dimensional Zn(II)-porphyrin@GO nanohybrids.

For the synthesis of the free-base porphyrin (compound 10) and Zn(II)-porphyrin (compound 11) on a milligram scale which is suitable for further synthetic manipulations, the general reaction scheme devised by Twyman and Sanders\textsuperscript{19} was adapted and used in this project as described in Experimental section (Chapter 7). This method involved 1-iodohexane, pentane-2,4-dione and benzyl 3-oxobutanonate as the starting materials.\textsuperscript{20} The hexyl derived pyrrole was used as the basic building unit to build up this type of porphyrins.\textsuperscript{21, 22} The porphyrin side groups and the metal centre were tuneable to incorporate several substituents according to future photovoltaics generation. The Zn(II)-porphyrin (compound 11) has been chosen as it incorporates four hexane chains on the side of the macrocycles ring in order to get a better solubility in some common organic solvents, such as toluene and chloroform. As found in Figure 3.11 in Chapter 3, the Zn(II)-porphyrin (compound 11) molecules are oriented face-on and show two alkyl chain groups placed anti with respect to the aromatic core. Thus, the supramolecular structure of Zn(II)-Porphyrin (compound 11) shows weakly linked tubular arrangements of the porphyrin planes in their solid state.
Similarly to the case discussed in Chapter 4, in this section of the project, the thioacetate-protected Zn(II)-porphyrin (compound 11) was synthesised and also used in fresh solutions in order to avoid the de-protection over time and the formation of a disulphide bridge by dithiol porphyrin coupling. As stated before, this was necessary as the formation of such dimers in the presence of oxygen and aqueous environments is likely due to form additional π-π interaction between porphyrin dimer and GO and allow for uncontrolled stacking, thus altering the optical properties of the emerging nano-composite. Protection unit -OAc groups ensure the preservation of a non-covalent monomeric porphyrin unit ready for a controlled donor-acceptor interlayer association with the GO.

Figure 5.1: Schematic diagram presents the generation of Compound 11@GO complex.
Figure 5.1 shows the schematic diagram of generation of compound 11@GO complexes. Since the graphene oxide was prepared by the Hummers’ method, oxygen containing groups such as hydroxyl, epoxyl, carboxyl and other carbonyl groups were likely present on the edge or on the surface of the graphene oxide. As a result, when treated with sonication (30 min), graphene oxide can be efficiently exfoliated from graphite oxide. Graphene oxide and Zn(II)-porphyrin molecules were mixed in ethanol and stirred for 24 hours under room temperature. The resulting compound 11@GO nanohybrid material formed stable dispersions in ethanol (without precipitations over several weeks) and have been characterised by spectroscopic methods such as UV-vis, FT-IR, Raman in the dispersed phase. The treatments of as-made GO with the thioacetate porphyrins resulted in the decoration of the surface of the graphene oxide likely though concentrated supramolecular interactions, and gave rise to new nanohybrids denoted compound 11@GO. The compound 11@GO complex was formed by π-π stacking between the pyrrole rings of the Zn(II)-porphyrin (compound 11) and the hexagonal rings on the graphene oxide sheets, likely reinforced by hydrogen bonding between -COOH or -OH groups of the GO and the -C=O unit of the thioacetate group.

The morphology information of compound 11@GO nanohybrid was compared to that of the original GO determined by AFM and TEM coupled with selected area electron diffraction (SAED). Steady-state and time-resolved fluorescence emission studies have been carried out to probe whether an energy transfer process occurred between graphene oxide nano-flakes and the Zn(II)-porphyrin (compound 11).
5.2.1.1. Solid state investigation by TEM

Figure 5.2: (a) TEM image of GO, the scale bar=200 nm; (b) Selected area electron diffraction (SAED) of graphene oxide incorporated with Figure 5.2 (a); (c) TEM image of compound 11@GO complex, the scale bar=500 nm; (d) TEM image (the magnified area from the same measuring sample with figure 5.2 (c)) of compound 11@GO complex, the scale bar=50 nm; (e) Energy-dispersive X-ray spectroscopy (EDX) analysis of compound 11@GO
A typical TEM image of GO was shown in Figure 5.2 a, and it can been seen that the size of GO nanoflakes which were used in compound 11@GO generation was reasonably large, around one micrometre, and there were no obvious holes or defects observed on the GO surface analysed. The edge of GO sheet indicated the fact that the graphene oxide sheet was a mono-layered structure or it is a few-layer uniquely overlapped structure. Figure 5.2 b is the selected area electron diffraction (SAED) with the same area in figure 5.2 a. The SAED pattern of GO indicated a crystalline structure. The SAED data suggested that the graphene oxide sheets were not randomly oriented with respect to each other and that the physical properties of each layer within the GO sheets were unique (the interlayer coherence is not destroyed by complexation). From Figure 5.2 (c) and (d), the TEM image showed the fact that after complexation with Zn(II)-porphyrin, the graphene oxide sheets form a uniform, multi-layer compound 11@GO composite structure. As shown in Figure 5.2 c, after complexation with Zn(II)-porphyrin, the graphene oxide sheets were aggregated together and formed an overlapped composite. The compound 11@GO complex was still kept at micrometre dimension. Figure 5.2 (d) is the magnified TEM image of compound 11@GO complex from the same area of figure 5.2 (c). Figure 5.2 (d) exhibited more detailed surface information of the compound 11@GO complex: the Zn(II)-porphyrin molecules were tightly attached on the whole surface of GO and it appeared that the Zn(II)-porphyrin formed a highly ordered structure. The morphology information of the highly ordered structure can be further analysed by AFM. As shown in Figure 5.2 (c) and (d), the structure of the compound 11@GO complex did not present any obvious hole or defects on its surface. This is means that the controlled sonication time (15 min) introducing to disperse GO did not damage the GO structure. Meanwhile, the dispersed GO phase also led to a reactive surface which allowed free Zn(II)-porphyrin (compound 11) molecules to attach by π-π stacking interaction likely reinforced by Zn-O bond. The EDX characterisation, Figure 5.2 (e), indicated the presence of Zn elements and the complexation of the complex structure of the Zn(II)-porphyrin with GO. The presence of Cl element may come from the synthesis of GO process. More TEM images of compound
11@GO complex are presented in the Appendix ix, Figure B.9.

5.2.1.2. Solid state investigation by AFM

Tapping mode AFM (TM AFM) was carried out to identify the morphology information of the Zn(II)-porphyrin (compound 11). The TMAFM measurement of Zn(II)-porphyrin sample was prepared by using a spin coating at 3000 rpm which allowed the deposition of the Zn(II)-porphyrin solution (1 μM) onto a 2 cm² Mica substrate.

**Figure 5.3:** (a) 3D TMAFM image of Zn(II)-porphyrin (compound 11@GO) self-assembly on a Muscovite Mica substrate by using a spin coating at 3000 rpm; (b) Tapping mode AFM image of Zn(II)-porphyrin self-assembly crystal, the insert is the image of 2-dimensional FFT; (c) Profile analysis showing the heights of line area in Figure 5.3 b.
Figure 5.4: (a) 3D TMAFM image of compound 11@GO by dropping complex solution onto an O3 modified HOPG substrate; (b) TM AFM image of compound 11@GO complex, the insert is the image of two dimensional FFT; (c) profile analysis showing the heights of line area in Figure 5.4 b

It can be seen from Figure 5.3 (the TMAFM image and FFT data) that the Zn(II)-porphyrin (compound 11) did not wet the Muscovite Mica surface well, it dried to
form uncrystallised islands the heights of which are around 10 nm. Those islands were due to a self-assembly process between the platform of the pyrrole structure within the Zn(II)-porphyrin and the conjugated area by \( \pi-\pi \) stacking. From the profile analysis, (Figure 5.3 (c)), the heights of those “islands” are around 10 nm and some of them can be up to 40 nm. This may due to the specific designed long chain of Zn(II)-porphyrin (compound 11), those long chains can interact with each other and form a relatively stable structure.

The TMAFM image of compound 11@GO complex was generated by dropping complex solution onto an Ozone modified HOPG substrate. The ozone-modified HOPG substrates need to be freshly prepared to avoid any possible impurities contaminations on its surface.

From Figure 5.4, it can be found that after the complexation with GO, Zn(II)-porphyrins (compound 11) form some regular semi-triangular highly ordered structures. The insert FFT (Figure 5.4 (c)) exhibits that this regular semi-triangular structure is crystalline, which confirms the hypothesis from the TEM images (that a complex is formed). From Figure 5c, the file of heights of distribution curve analysis, it can been seen that the heights compound 11@GO are around 2-3 nm. Considering the height of a single GO sheet as 0.8 nm to 1 nm\(^2\) and the contribution from the grafted Zn(II)-porphyrin (compound 11) crystals, the images obtained are representative of single- and/or bilayered exfoliated GO material. The TMAFM images of the compound 11@GO complex also indicated that the Zn(II)-porphyrin (compound 11) was uniformly and regularly coated onto the whole surface area of GO. The difference between island-like Zn(II)-porphyrins and semi-triangular Zn(II)-porphyrin crystals can be regarded as a consequence of the adsorptive interaction between Zn(II)-porphyrins (compound 11) with graphene oxides through \( \pi-\pi \) stacking and the formation of a new compound 11@GO complex.
5.2.1.3. **Raman spectroscopic characterisation**

![Raman Spectroscopy Graph](image_url)

**Figure 5.5**: Raman spectroscopy of GO and compound 11@GO complex measurements.

As stated above, Raman spectroscopy is widely used tool in characterisation of carbon nanomaterials by giving its ability to inform on vibrational and other low-frequency modes in such materials systems.\(^{24,25}\) The Raman spectra shown in figure 5.5 were recorded from the samples dispersed in ethanol with a \(\lambda_{ex} = 514\) nm (a region of the emission spectra of the compound 11@GO without limited interference from fluorescence emission of Zn(II)-porphyrin). During the measurement, the laser may cause some damages to the extended fragile network.

It can be found from Figure 5.5 that the intact GO exhibited a D band at 1350 cm\(^{-1}\) due to its oxidised defects on its sheet edge and some disordered carbons on its surface.\(^{26}\) It also shown a G band at 1599 cm\(^{-1}\), which corresponded to the sp\(^2\)-bonded carbon structure.\(^{26}\) The I\(_D\)/I\(_G\) ratio of the intact GO is 0.834. This relatively higher I\(_D\)/I\(_G\) indicated the fact that the GO has a lower degree of crystallinity with respect to other known of graphite materials.\(^{27}\)
After mixing the GO and Zn(II)-porphyrin (compound 11), π-π stacking interaction can occur between Zn(II)-porphyrin (compound 11) and GO sheets. Comparing the Raman spectra of compound 11@GO complex with related spectra of the intact GO used hereby, it was found that the D band of compound 11@GO complex is at 1350 cm\(^{-1}\), while the G band of compound 11@GO complex is shifted slightly down to 1596 cm\(^{-1}\). This might be due to the decreasing number of layers in their solid states caused by the prolonged sonication treatment introduced into the system. Another possible reason for the shift could be that after the complexation, the long alkyl chains present within the structure of compound 11 made the complex system more soluble in ethanol, and the resulting composite material therefore dispersed better in ethanol. When comparing the two spectra together, there were some subtle changes which could be observed. Over interpretation is that the complexation process did not cause any significant damage to GO sp\(^2\)-bonded carbon structure and thus the electron and mechanical properties of GO sheets should be retained upon complex formation.

The \(I_d/I_g\) ratio of compound 11@GO complex is 0.817. This decreasing \(I_d/I_g\) ratio suggest that the compound 11 were successful bonded to GO surface and this system contribute to a the re-informant of the conjugated graphene network.\(^{28}\) The Zn centre in compound 11 may also bind to the -O- functionalities from the surface of the GO during the complexation progress by forming a Zn-O dative bond. This kind of interaction may also result in decreasing of the \(I_d/I_g\) ratio as the aromatic molecular compound 11 will be closely attached to the sp\(^2\) surface. However, such hypothesis would need to be reinforced by more detailed structural investigations may involving small molecule X-ray crystallography, if a single crystal of a simple GO fragment and compound 11 could be co-crystallised. So far, this structure was not obtained during this project.

5.2.1.4. Two-dimensional fluorescence contour plotting fluorescence imaging characterisation

Two-dimensional fluorescence contour plotting of free graphene oxide (Figure 5.6 a) and of compound 11 (Figure 5.6 b) were recorded separately (\(\lambda_{\text{excitation}}\) from 200 nm to 800
nm, $\lambda_{\text{emission}}$ from 200 nm to 800 nm, spectra recorded every 10 nm) to investigate the excitation and fluorescence emission behaviour of compound 11 and GO.

**Figure 5.6** (a) Two-dimensional fluorescence contour plotting of free GO in ethanol (0.5 mg/mL). (b) Two-dimensional fluorescence contour plotting of free Zn(II)-porphyrin (compound 11) in ethanol (0.01 mg/mL).
As shown in Figures 5.6 a, two prominent diagonal lines were observed due to the Rayleigh scattering (first and second order). It presented the fact that in the GO solution, the electrons in the state energy levels of the GO sheets were excited and emission occurred at the same wavelength, which means that there were no fluorescence behaviour in GO solution. From figure 5.6 b, a strong range of emission peaks (in the interaction ranging from 580 nm to 670 nm) was observed. This strong emission from compound 11 was due to the conjugated, electron-rich, structure of the porphyrin network incorporating Zn-N bands, as well as the expected porphyrin Soret bands.

**Figure 5.7**: Two-dimensional fluorescence contour plotting of pure graphene oxide (0.5 mg/mL) and Zn(II)-porphyrin (0.01 mg/mL) mixture in ethanol.

Two-dimensional fluorescence contour plotting for compound 11@GO (Figure 5.7) were recorded ($\lambda_{\text{excitation}}$ from 200 nm to 800 nm, $\lambda_{\text{emission}}$ from 200 nm to 800 nm) to investigate the excitation and emission behaviour of compound 11 before and after complexation with GO. It can be found that after interacting with GO, nearly all free porphyrins were attached onto the GO surface. The strong Zn(II)-porphyrin emission peak disappeared almost entirely in the compound 11@GO complex contour plot. The complexation process inferred by the disappearing peak also corresponded with the TEM and AFM results. The fluorescence plot also shows that the emission wavelength of the
peak maximum, experience a red-shift (from 580 nm – 670 nm to 620 nm - 670nm). In additional, a severely quenched has been observed after the compound \( \text{II} \) were interacted onto graphene oxide sheet surface.

Those red-shifts and quenching behaviours were due to the consequences of the \( \pi-\pi \) donor-acceptor interaction which linked compound \( \text{II} \) with graphene oxide and there was also an energy transport process occurs from the singlet excited state of compound \( \text{II} \) to GO. The fluorescence quenching can be a result of electron transfer, spin-orbit coupling or intersystem crossing to the excited triplet state finally causing the return to the ground state of compound \( \text{II} \). Another reason for this quenching is that in compound \( \text{II}@GO \) complex system, GO was a non-fluorescent molecule and could be used as a fluorescence quencher. The energy transport between compound \( \text{II} \) and GO might cause by the exited electrons transferred from compound \( \text{II} \) to graphene oxide sheet. From figure 5.7, it can be found that the two Rayleigh scatter line were still presented in the plot and there were subtle changes compared to GO two dimensional contour plotting: this suggests that the optical properties of GO are remained in the complex system.

### 5.2.1.5. UV-vis spectroscopy titration of Zn(II)-porphyrin (compound \( \text{II} \)) and Graphene oxide

In order to further analyse the compound \( \text{II}@GO \) complex’s optical absorption, GO and Zn(II)-porphyrin titration measurements were carried out by using UV-visible spectroscopy. Figure 5.8 a shows the optical absorption spectra of compound \( \text{II} \) dispersed in ethanol (3 mL, 1\( \mu \)M), then titrated with Zn(II)-porphyrin (1 \( \mu \)M) and graphene oxide (0.05 mg/mL) ethanol solution. In this experiment, a stock solution of Zn(II)-Porphyrin (1\( \mu \)M) and graphene oxide (0.05 mg/mL) were prepared in a ethanol. Separately, a solution of Zn-Porphyrin (1\( \mu \)M) was also prepared in a ethanol solution. Stock solution was gradually added into the cuvette containing Zn-Porphyrin, so that the concentration of Zn-Porphyrin for each UV-Vis experiment was kept constant.
Figure 5.8: (a) the optical absorption spectra of Zn(II)-porphyrin (compound 11) dispersed in ethanol (3 mL, 1μM), then titrated with Zn(II)-porphyrin (1 μM) and graphene oxide (0.05 mg/mL) ethanol solution, (Magnified relevant region of secondary absorbance band, from 510 nm - 660 nm, can be found in Appendix H); (b) UV-visible absorption normalised intensity with respect to added volume of the GO in compound 11.

It can be seen from figure 5.8 that the main compound 11 absorbance peak located
at 416 nm. This peak was then enhanced after the addition of GO solution. For the secondary absorbance peak at 576 nm, similar enhanced behaviours were also observed. From Figure 5.8 b, it can be found that the enhanced absorption behaviour of compound 11 was logarithmically increased with the concentration of GO in the system. This enhanced UV-visible absorbance was due to a consequence of the energy transferred between compound 11 and GO and the complexation of compound 11@GO complex.

Same measurement conditions (compound 11 was dispersed in 3 mL of ethanol to give a 1μM concentration solution, then titrated with compound 11 1 (μM) and graphene oxide (0.05 mg/mL) as an ethanol dispersion) were also applied to compound 11 and GO Fluorescence spectroscopy measurement with λex=346 nm, shown from Figure. 5.9. From the measured result, the main emission peak at 438 nm was quenched with the addition of graphene oxide solution. Figure 5.9 b presented the normalised emission intensity with respect to the added volume of the GO.
Chapter 5 Results and Discussions

Figure 5.9: (a) Fluorescence emission quench behavior of Zn(II)-porphyrin@GO; (b) emission normalised intensity with respect to added volume of the graphene oxide.

The fluorescence quenching and UV-visible enhancement confirmed the fact that after complexation, the compound 11 and GO complex presented stronger light absorption ability (less energy loss) compared with pristine compound 11 molecule. This is an improvement if the ultimate goal of employing this complex as a material appropriate for photovoltaic applications. However, neither UV-visible titration measurement nor two-dimensional contour plotting fluorescence measurements were able to explain the exact energy transfer form, a hypothesis was proposed that after exited by a quantum of energy, the electrons in the ground state of compound 11 were excited to a higher energy
level and then transferred to the graphene oxide. However, further studies by DFT calculations are needed to identify the precise electronic transitions involved and electrons configuration of the system.

5.2.1.6. Spectroscopic characterisation by FTIR

Fourier transform infrared spectroscopy was applied in this project to identify the different type of bonds appeared in compound 11@GO complex. From the GO FTIR spectrum (black line) prior to the complexation, the bands at 1095 cm\textsuperscript{-1} and 1759 cm\textsuperscript{-1} are due to C=O stretching vibrations from carbonyl and carboxylic groups and the band located at 1612 cm\textsuperscript{-1} is due to C-OH stretching vibration. FTIR spectroscopy thus provided a direct evidence of the presence of an abundance of different types of oxygen containing groups on the GO surface.

![Figure 5.10: FTIR spectra of GO, Zn(II)-porphyrin and Zn(II)-porphyrin@GO.](image)

From Figure 5.10, that the peak at 881 cm\textsuperscript{-1} for compound 11 (blue line) almost disappeared compared to the compound 11@GO complex spectrum (red line). In contrast, in the compound 11@GO spectra, a new broad band emerged at 1264 cm\textsuperscript{-1}, which
corresponds to the C-N stretching band of the amide group. The peaks at 1456 cm\(^{-1}\), 1495 cm\(^{-1}\) and 1630 cm\(^{-1}\) were the representation of carboxylate groups. The peak at 1711 cm\(^{-1}\) is assignable to the C=O stretching vibration. The peak at 3458 cm\(^{-1}\) was due to the water appearance in the measured sample. Additionally, all bands which appeared in the spectrum of in compound \(11@\text{GO}\) nano-complex were also obtained in the spectra of GO or in that compound \(11\), which suggests that no new chemical bond was formed during this complexation. This implies that complexation was due to a non-covalent linkage, which occurred in the system. In summary, FTIR results suggest a successful non-covalent attachment of GO and compound \(11\), and points towards formation of a supramolecular nano-hybrid formation.

5.2.1.7. Fluorescence life time characterisation by single-photon fluorescence spectroscopy

![Fluorescence spectroscopy](image)

**Figure 5.11:** Fluorescence spectroscopy by time-controlled single-photon counting \(\text{Zn(II)-porphyrin and Zn(II)-porphyrin}@\text{GO}\) (under \(\lambda_{ex}=473\) nm, \(\text{Zn(II)-porphyrin}\) 1 \(\mu\)M disperse in ethanol, \(\text{Zn(II)-porphyrin}@\text{GO}\) complex dispersion contain 1\(\mu\)M porphyrin and 0.1 mg/mL graphene oxide).
Fluorescence spectroscopy suing time-correlated single-photon counting (TC SPC) was used to further study the interactions in the excited state (dispersed phase and thin film) between GO and compound 11. From Figure 5.11, the fluorescence decay time profiles show that the fluorescence lifetimes of photo-excited compound 11@GO complex were fitted onto multi-components experiential function to give lifetime component of 813 ps (75.2%) and 3703 ps (24.8%) with $\chi^2 = 1.27$. The complex system contains two components, it was reasonable to assume that the first component 3703 ps was a fingerprint of the presence of compound 11, and the second component 813 ps was indicated the fact that the fluorophore lifetime of porphyrin appearing in an environment of graphene oxide matrix. Both of those fluorescence lifetimes were dramatically modified compared to that of the intact compound 11 (which is 6804 ps, 100%) and the decreased fluorescence lifetime was about 46%. The measured fitted curve correspond to a $\chi^2=1.27$ in compound 11@GO complex and a $\chi^2=1.22$ in the compound 11 measurement, so in both cases the fitting was deemed reliable. Data suggest that complexation occurred.

### Table 5.1: Data of compound 11 and compound 11@GO single-photon fluorescence lifetime.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{ex}$</th>
<th>$\chi^2$</th>
<th>$\tau_1$ %</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ %</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 11</td>
<td>473 nm</td>
<td>1.22</td>
<td>100</td>
<td>6804</td>
<td></td>
<td></td>
</tr>
<tr>
<td>compound 11@GO</td>
<td>473 nm</td>
<td>1.27</td>
<td>75.2</td>
<td>813</td>
<td>24.8</td>
<td>3703</td>
</tr>
</tbody>
</table>

As a result of the dramatic decrease in fluorescence decay lifetime measured in the nanohybrid system, it was reasonable to assume that there was a charge-separation and/or energy transfer process taking place between the compound 11 and GO in the rebuilding complex. In addition, this result also supports and corroborates the efficient emission quenching of the Zn(II)-porphyrin in the presence of GO in the dispersed phase.
5.2.1.8. Confocal fluorescence microscopy

![Confocal fluorescence microscopy images](image)

**Figure 5.12**: Single-photon laser confocal fluorescence of a thin film obtained by drop-casting a solution of nanohybrid (1 μM) onto borosilicate glass: (a) solid compound 11@GO composite, intensity image; the measured area is 30 μm × 30 μm (b) lifetime mapping and scale bar.

![Fluorescence lifetime distribution curve](image)

**Figure 5.13**: Corresponding fluorescence lifetime distribution curve with life time mapping of compound 11@GO complex. (Figure 5.12b)
Figure 5.12 (a) and (b) show the lifetime emission maps of the solid-state compound 11@GO complex and the single-photon induced fluorescence intensity maps. The measured data corresponded to the spatial variations in compound 11@GO complex fluorescence emission lifetimes. From Figure 5.13, the major lifetime components measured for the compound 11@GO complex ranged between 2000-5000 ps into a very broad FWHM (full width at half of the maximum). A comparatively broader FWHM of the statistical distribution (around 3000 ps) indicated the low homogeneity of the fluorescence decay. This was due to the formation of the nano-hybrids structure of overlaying morphologies in the thin film.

5.2.1.9. Conclusion

Compound 11 and GO were non-covalently assembled and a new Compound 11@GO complex material has been synthesised. This constituted an important setup in the materials synthesis following on from the oxidation of graphite and GO formation, and subsequent supramolecular functionalisation with compound 11 especially selected on basis of its bulkiness and solubility in organic solvents. The structure and morphology information of compound 11@GO complex have been studied by AFM and TEM coupled with SAED. It can be found that compound 11 formed nano- crystalline structures when deposited onto the surface of GO, which are different morphology-wise when compared to those resulting after the self-assembly of the free compound 11. Raman spectroscopy give the inner geometry and atomic structure of GO and compound 11@GO complex. FT-IR characterisation confirmed that the complexation of compound 11 and GO occurred. From the fluorescence quenching and florescence lifetime decay behaviour, it was suggested that a strong energy transfer occurred between compound 11 and GO. The transferred energy was likely from compound 11 to GO, for which can be potentially used in the a novel optoelectronic devices, but further TD DFT calculations could be needed to establish this into precision.
5.2.2. Three-Dimensional porphyrin@rGO composite.

5.2.2.1. Synthesis approaches.

The general synthesis of 3-dimensional porphyrin@rGO composite was carried out by a one-pot hydrothermal reaction. Different types of porphyrin molecules were dissolved in chloroform (1 mM) and then mixed with the GO ethanol dispersion. The mixture was then transferred into a Teflon liner ready for autoclave synthesis, which was placed into a stainless steel hydrothermal vessel (autoclave). To avoid the generation of an extremely high internal pressure, the total volume added into the steel vessel was controlled to be under 10 mL as the internal volume of the autoclaves used in this project was of 15 mL. The autoclave was then transferred into a furnace which was held at a temperature of 200 °C for 24 hours. After the reaction was deemed completed, the autoclaves were cooled down to room temperature. The mixture recovered from the resulting dispersion was characterised by TEM and SEM. It is believed that the process resulted with a 3-dimensional cylinder-like structured composite.

In porphyrin@rGO composite synthesis, the solvent combination (chloroform and ethanol) was chosen due to the fact that those two organic solvents can fully dissolve or disperse all starting materials and make a homogeneous mixture in those solvent. The processing GO in a water suspension (0.5 mg/mL) was also tested instead of the GO ethanol solution, and microscopy showed that similar results. Different reaction temperatures (160 °C and 180 °C) were also tested, but 200 °C was deemed due to a better ability to lead to the reducing of GO, and the heightened inner pressure generation inside autoclave.
Figure 5.14: Molecule structure of (a) meso-Tetraphenylporphyrin, compound 13; (b) 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin, compound 14; (c) 5,15-Di(3-acetylthiomethylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin, compound 10 and (d) digital picture of the material recovered after autoclaving and which containing the resulting compound 13@rGO composite.

There were three types of porphyrin successful applied in this composite synthesis process (see Figure 5.14 above): meso-Tetraphenylporphyrin, (compound 13) 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (compound 14) and 5,15-Di(3-acetylthiomethylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrin (which is the free base porphyrin synthesised hereby, compound 10). The molecule structures of those porphyrins were shown in Figure 5.14 compound 13 is a sample of a
commercially available, simple porphyrin. Compared with compound 13, all the phenyl
groups at the periphery of the porphyrin core of compound 14 shows compact substituted
all hydrogen atoms by fluorine. This was deliberately chosen as it is a highly
electronegative atom, which reduces the π-electron delocalisation in the phenyl rings and
exhibit more fluorescence behaviour. Compound 10 (which was referred to in Chapter 3 as
the free base porphyrin) is the metal free porphyrin variant of compound 11. The study of
the compound 10@rGO composite was hoping to set up a bridge to link the observations
from the synthesis of the 2-dimensional compound 11@GO nanohybrids and
3-dimentional compound 10@rGO composite and be able to compose the resulting
nanohybrids morphologies.

5.2.2.2. Solid state investigation by TEM

The TEM measurements of porphyrin containing rGO composites were carried out
on samples resulting by drop-casting the composite dispersion onto lacy carbon TEM grids. Figure 5.15 shows the TEM images of compound 13@rGO composite (a), compound
14@rGO composite (b) and compound 10@rGO composite (c). From the TEM images, it
can be observed that the three different composite materials all show similar structures on
the nanoscale, the porphyrins incorporated present as black dots with dimensions range
from 1-5 nm onto the rGO surface.
Figure 5.15: TEM images of (a) compound 13@rGO composite, the scale bar=50nm, (b) compound 14@rGO composite, the scale bar=50nm (c) compound 10@rGO composite, the scale bar=100nm.

Comparing the surface morphology of the composites shown in Figure 5.15 with the 2-dimensional compound 11@GO nanohybrids, the black dots assign to porphyrins present in the 3D composite materials appear to be randomly attached onto the rGO surface, but in the 2D nanohybrids, the compound 11 covered the whole surface of GO. A reasonable explanation for the randomly dispersion may be because because the high temperature and inner pressure generated within the Teflon liner prevented the free porphyrins...
molecules to deposite uniformly onto the rGO and attached strongly at the defect sites of the GO.

5.2.2.3. Solid state investigation by Field Emission SEM

**Figure 5.16:** SEM images of compound 13@rGO composite at different magnifications, the scale bar is 100 μm (left) and 10 μm (right) respectively.

**Figure 5.17:** SEM images of compound 14@rGO composite at different magnifications, the scale bar is 100 μm (left) and 10 μm (right) respectively.
The SEM measurements of porphyrin and rGO composite were carried out on samples generated by freeze drying composite samples to remove forces of solvents, and then transferring the solid samples onto a HOPG substrate. Figure 5.16, 5.17, 5.18 show Field Emission SEM images of the three porphyrin@rGO composites analysed. The samples ready for microscopy were further freeze dried to avoid any structure change during the measurement. The SEM images suggested morphologies consistent onto a 3-dimensional structure of the synthesised composites in solid state. The hydrothermal reduced graphene oxide sheets formed a micro porous network structure, whereby the hole sizes obtained in compound 13@rGO composite ranged from 2 μm to 5 μm, while the hole size of compound 14@rGO composite showed a slight difference: the range were from 0.5 μm to 5 μm. The hole size of the compound 10@rGO composite showed a dramatic decrease compared with the other two composites, the surface morphology of the compound 10@rGO became more dense, with reduce smaller-sized network. The reason for this change remains to be determined: it is assignalbe to the effect that the different sizes of porphyrin molecule and the presence of four long carbon hexyl chain on the edge of compound 10, which may interrupt to the formation of those structure. The morphology of these composites is likely important in solar cells materials generation.
5.2.2.4. Spectroscopic characterisation by Raman

Figure 5.19 The Raman spectroscopy of hydrothermally reduced rGO, compound 13@rGO composite, compound 14@rGO composite and compound 10@rGO composite-selected range of the spectra.

Figure 5.19 shows a selected range of the Raman spectroscopy measurements of hydrothermal rGO, compound 13@rGO composite, compound 14@rGO composite and compound 10@rGO composite. The hydrothermal reduced graphene oxide exhibited a D band at 1348 cm\(^{-1}\) and a G band at 1592 cm\(^{-1}\). The I\(_D\)/I\(_G\) ratio was estimated at 0.917. For compound 13@rGO composite, a D band at 1350 cm\(^{-1}\) and a G band at 1594 cm\(^{-1}\) were recorded with a I\(_D\)/I\(_G\) ratio of 0.908. The compound 14@rGO composite exhibited a D band at 1353 cm\(^{-1}\) and a G band at 1596 cm\(^{-1}\). Whereas the compound 10@rGO composite presented a D band at 1350 cm\(^{-1}\) and a G band at 1596 cm\(^{-1}\). The I\(_D\)/I\(_G\) ratio of free base porphyrin@rGO composite is 0.807. A comparison of this data can also be found in Table 5.2. Comparing the Raman spectroscopy of these porphyrins@rGO composite with that of the hydrothermal rGO starting materials, it can be observed that the D band peaks and G band peaks occurs in similar position, and the I\(_D\)/I\(_G\) ratios also remain very close in value. This is the case with the exception of the compound 10@rGO composite, which presented
the lowest $I_D/I_G$ ratio. The Raman measurements of all these porphyrins@rGO composites indicated the fact that after the incorporation of the selected prophyrrins, the main inner graphitic carbon $sp^2$ of rGO structure remains largely unaltered.

**Table 5.2:** Table of $I_D/I_G$ band intensity of reduced graphene oxide and different types of porphyrins composites. (Each spectra average of 3 times at measurement, $\pm$ 10%)

<table>
<thead>
<tr>
<th>Materials</th>
<th>D band (cm$^{-1}$)</th>
<th>$I_D$</th>
<th>G band (cm$^{-1}$)</th>
<th>$I_G$</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce Graphene Oxide (rGO)</td>
<td>1348</td>
<td>20641</td>
<td>1592</td>
<td>22518</td>
<td>0.917</td>
</tr>
<tr>
<td>compound 13@rGO</td>
<td>1350</td>
<td>18947</td>
<td>1594</td>
<td>20863</td>
<td>0.908</td>
</tr>
<tr>
<td>compound 14@RGO</td>
<td>1353</td>
<td>10936</td>
<td>1596</td>
<td>11498</td>
<td>0.951</td>
</tr>
<tr>
<td>compound 10@RGO</td>
<td>1350</td>
<td>14784</td>
<td>1596</td>
<td>18316</td>
<td>0.807</td>
</tr>
</tbody>
</table>

5.2.2.5. Confocal fluorescence microscopy imaging

To investigate the formation of the porphyrins@RGO composites in thin film, solid state single-photon laser confocal fluorescence measurements coupled with FLIM were carried out. Figure 5.20 shows the lifetime emission maps of solid-state compound 13@rGO composite, measured under excitation with a laser of $\lambda_{ex}$=405 nm. The single-photon intensity maps (Figure 5.20 a) show the spatial variations in fluorescence emission and the lifetime imaging maps (Figure 5.20 b) across the film, Figure 5.20 c was the corresponding distribution curve for the FLIM image and also shown the predominant lifetime component ($\tau_1$) for compound 13@rGO composite.
Figure 5.20: Single-photon laser confocal fluorescence of a thin film obtained by dedrop casting a solution of nanohybrids onto borosilicate glass: (a) solid compound 13@rGO composite, intensity image under $\lambda_{ex}=405$ nm, the measured area is $30 \, \mu m \times 30 \, \mu m$ (b) lifetime mapping and scale bar and (c) corresponding fluorescence lifetime distribution curve with life time mapping.

From the compound 13@rGO composite solid state life time measurement, the main lifetime observed in the corresponding lifetime distribution curve was $2400 \pm 100$ ps. The range of FWHM (full widths at half highest) measured for this composite was
approximate from 2200 ps to 2650 ps. The 430 ps FWHM means the compound 13@rGO composite has a rather low homogeneity of fluorescence lifetime decay, which was reasonably to assume due to the formation of a nanohybrids structure and differing scattering corresponding to aggregates of dimensions across the film.

![Image](a) ![Image](b) ![Image](c)

**Figure 5.21**: Single-photon laser confocal fluorescence of a thin film obtained by dedrop casting a solution of nanohybrid onto borosilicate glass and drying under air: (a) solid compound 14@rGO composite, intensity image under $\lambda_{ex}=405$ nm, (b) lifetime mapping and scale bar and (c) corresponding fluorescence lifetime distribution curve corresponding to the with life time mapping image (b).
Figure 5.21 presents the solid state single photo laser confocal fluorescence measurement results of compound 14@rGO composite. The intensity map presented in figure 5.21 (a) indicating the spatial variations in fluorescence emission. The lifetime mapping presented at figure 5.21 (b) is the lifetime mapping and coloured scale bar. Compared with other composite materials lifetime mapping, the compound 14@rGO composite exhibits areas of intense fluorescence emission in both intensity image and FLIM mapping, the reason for this is likely due to the fact that fluorine groups on the edge of compound 14 presented very strong fluorescence emissions then required obscure measuring atmosphere. Figure 5.21 c was the lifetime distribution curve corresponding with lifetime mapping in Figure 5.21 b, it can be found that a main fluoresce lifetime recorded in compound 14@rGO composite material was 1730 ±100 ps.

Compared with compound 13@rGO composite, the whole composite lifetime range exhibited a huge increasing which from 1000 ps to 2000 ps (2010 ps – 3088ps; 799 ps - 2846 ps). Compound 14@rGO composite also presented a relatively broader FWHM (full width at half of the maximum), which is around 400 ps, this confirmed a low homogeneity of fluorescence decay and hybrids structure formation.
Figure 5.22: Single-photon laser confocal fluorescence of a thin film obtained by dedrop casting a solution of nanohybrid onto borosilicate glass: (a) solid state compound 10@rGO composite, intensity image, the measured area is 30 μm × 30 μm (b) lifetime mapping and scale bar and (c) corresponding fluorescence lifetime distribution curve with life time mapping.

The measurement of single-photon laser confocal fluorescence for compound 10@rGO was also carried out in solid state, for a thin film. From Figure 5.22 (a) shows the intensity fluorescence emission map, which gives the spatial variation information about compound 10@rGO composite, under an excitation wavelength of λ_{ex}=405 nm. The Figure
5.22 (b) and (c) are the lifetime mapping, with coloured time scale bar and corresponded fluorescence lifetime distribution curve. From the lifetime mapping and the corresponding distribution curve, it can be found that the main lifetime peak was at 2700 ± 100 ps. The FWHM (full widths at half of the maximum) was approximately 1700 ps, and with lifetime varies which from 2000 ps to 3700 ps. This relatively broad FWHM indicated a hybrids composite structure.

5.2.2.6. Summary to 3D porphyrin@rGO composite materials formation and attempted TGA investigations

We demonstrated a novel one-step method to synthesise 3-dimensional micro-porous porphyrins@rRO composite materials. The different types of porphyrin systems were graphed onto the surface of reduced graphene oxide sheets using hydrothermal methods. The newly formed composite nanohybrids retained a GO type structure in the solid state. The structure and surface morphology information of porphyrins@rGO composite were characterised by TEM and SEM. It can be seen from the measurements that tower-like systems were attached onto a 3-dimentional micro-porous rGO. The inner structure of porphyrins@rGO composites was investigated by Raman microscopy, the measuring result confirmed the remaining sp² carbon atom structure after the hydrothermal reaction. The solid state single photon laser confocal fluorescence measurements were carried out to check whether the fluorescence is retained and probe if any energy transfer behaviour within the porphyrins@rGO composite can be assessed. The measured results exhibited a low homogeneity of fluorescence decay and pointed towards the formation of a hybrid structure which retained the porphyrin. TGA measurements of porphyrins@RGO composite were also carried out, and TGA data which is presented in Appendix i and ii, Figure A.1 to figure A.5. From the recorded results, the reduced graphene and their composite presented an increased turning temperature from 180 °C to 580 °C which suggest that the hybrid is formed by multiple components. Overall, data collected helped to partly characterised new graphene-based hybrid materials possessing links with several different porphyrins, commercially available as well as those synthesised.
hereby. This 3-dimensionsal micro-porous solid structures offer advantages as future synthetic scaffolds towards the development of novel optoelectronic devices and long term photo-catalyst materials.

5.3. References to Chapter 5


(b) F. Cheng and A. Adronov, *Chem. Mater.*, 2006, 18, 5389-5391;  


Chapter 6 Conclusions and Future Work

In this PhD project, firstly several methods to purify a commercially-provided source of CVD-made (Thomas Swan, Elicarb®) SWNTs were addressed. It was demonstrated that strong acid wash can be applied to oxidise and purify this type of SWNTs but that the drawbacks of all oxidation processes used were the structure of SWNTs is enormously damaged, whilst there still remain some impurities. For further improvements, a microwave-assisted purification step, combined with acid wash to improve the multi-steps purification process was established. Another multi-steps purification was carried out by using adaptation of a published steam base method. The improved methods can remove most of the impurities, but due to the rather complicated progress, the purification processes normally afford the desired materials in low yields. Next, the Bingel reaction was applied to functionalise the surface of the resulted SWNTs. The synthesis and characterisations of graphene oxide was carried out by a exfoliate route from graphite oxide in the liquid phase, with the assistance of a prolonged sonication. Chemical reduction method and a high temperature thermally reduction method were applied to reduce the graphene oxide. This project showed that both of those two methods which were adapted from the literature gave the desired carbon nanotubes. In addition, a hydrothermal reaction was applied in one-step to give a self-assembled graphene oxide hydrogel with an extended 3D network.

Secondly, a laboratory-scale synthetic pathway towards the generation of free base porphyrin (compound 10) was chosen to have a high solubility in common solvents with respect to its stacking materials. The synthesis and purification procedure was modified and scaled-up with respect to the original synthetic route, and adapted to improve the final yield. The free base porphyrin was then metallated to generate the corresponding Zn(II)-porphyrin (compound 11). The metalation of free
porphyrin was carried out by a new metalation procedure, involving the use of a microwave reactor. The chemical and physical properties of both the free base porphyrin and Zn(II)-porphyrin were investigated using $^1$H NMR and UV-Vis/Fluorescence spectroscopy. The measured results confirmed that the designed porphyrins have all the necessary physical-chemical characteristics which allow them to be potentially applied as light harvesting molecular units in photovoltaic devices. In addition, to the Zinc(II) complex, Indium(III) and Gallium(III) were incorporated via the microwave route into free base porphyrin. Unlike the case of Zn(II), the characterisation of Ga(III) and In(III) species did not point out to mono-centre species formation.

As proposed in the project objective, the as-made Zn(II)-porphyrin was then employed to synthesise porphyrin@SWNTs complexes, by both a non-covalent linking strategy and a covalent linking strategy. To the best of author’s knowledge this was the first report in the literature of the use of this soluble, functionalised porphyrin to form a porphyrin SWNTs nanohybrid structure. The non-covalent linking strategy was carried out by relying on the possible $\pi-\pi$ interactions between SWNTs and Zn(II)-porphyrin. The covalent linking strategy was carried out by using Bingel reaction functionalised SNWTs, which allowed the of contained –SH groups linking with de-protected Zn(II)-porphyrin via disulphide bridges to the SWNTs. Spectroscopic measurements in the dispersed phase led to a novel method of investigation allowing us to further demonstrate that both linking strategies can be achieved: coronene was used in the characterisation as a competitive reaction reagent candidate, used to pull apart the non-covalently linked porphyrin off from the SWNTs surface. It was also demonstrated that in the newly formed porphyrins@SWNTs complexes, there was energy transfer between SWNTs and porphyrin molecules, which confirmed the energy transfer hypothesis developed from C$_{60}$@porphyrin complex system in our group’s previous work.
Furthermore, a new Zn(II)-porphyrin@GO complex material was synthesised hereby, following the oxidation of graphite and subsequent supramolecular functionalisation with a functional Zn(II)-porphyrin. This system was deliberately selected on basis of its solubility in organic solvents. The structure and morphology of this nanohybrid was studied by AFM and TEM techniques. Due to the \( \pi-\pi \) interactions between the Zn(II)-porphyrin and graphene oxide sheets, the porphyrin molecules formed a highly ordered structure on the surface of the graphene oxide layers, which were not previously reported in the literature. In this PhD project, a novel one-step method to synthesise a 3-dimensional microporous structure denoted rGO and porphyrins was also reported. This method can reduce the graphene oxide and assemble porphyrins onto it simultaneously. The 3D microporous structure of the rGO material is an ideal scaffold. To the best of author’s knowledge, the hydrothermal method carried out in the presence of porphyrin is also the first attempt in porphyrin@rGO composite generation.

Finally, the single photon fluorescence confocal measurements which are method typically applied in life science research area to identify imaging probe’s fluorescence behaviors in the microscopic environment of living system were employed hereby. In this project, the advantages of this method to measure the fluorescence behaviour of porphyrins complexes/nanohybrids in thin film were used. Thus, this method can be used to investigate the energy transfer between porphyrin molecules and carbon nanomaterials in thin films, by carrying out lifetime imaging on a microscopic level.

The interactions of porphyrin molecules and nanomaterials were fully studied by spectroscopic methods such as UV-Vis and fluorescence. These findings about porphyrin complex/nanohybrids provide some insights into possible applications in photovoltaic devices constructions. Thus, future work will be carry out in celebration with Prof LinHong at Tsinghua University, China, who specialise in building and
Chapter 6 Conclusions and Future Work

testing real photovoltaic cells based on the newly synthesised porphyrin@carbon nanomaterials nanohybrids. A general technique of dye-sensitised solar cells production was learnt during a short training stage in Prof Lin Hong’s research group, and this was described in experimental section and Appendix.

The overall findings from this work suggest that if the newly generated materials could be incorporated in PVs, these cells could perform a better power conversion efficiency. Once the mechanism of newly generated PVs cells can be fully studied, the universal goal of applying new carbon nanomaterials into solar cells will have been fully achieved. Meanwhile, this thesis reports the synthesis and physical, chemical characterisation of a new family of carbon nanohybrids incorporating soluble porphyrins and single walled carbon nanotubes or graphene oxides.
Chapter 7 Experimental Section

7.1 General information

7.1.1 Chemicals and glassware

All solvents and chemicals applied in this PhD project were purchased from Sigma Aldrich Company Ltd and Fisher scientific. Unless specified, all solvents and chemicals used in all experiment section were reagent-grade and HPLC-grade and these were all directly applied without further purification.

There are two types of carbon nanotubes which were used in this project:

(1) Chemical Vapor Deposition (CVD) made Elicarb single walled carbon nanotubes: these are purified carbon nanotubes, now also available commercially. This particular batch was initially steam purified at the company site via a method developed by the Oxford Nanotube Group\textsuperscript{1,2,3} and was provided to us by Thomas Swan Ltd for this study, due to an ongoing collaboration with the Pascu Group.

(2) Electric Arc Growth method made Carbolex SWNTs, purchased as made from Carbolex Ltd. (Rice) and further purified.

Both of the SWNTs samples were available in their as-made state and therefore they contained some catalyst metal impurities and some amorphous carbon. Further purification was needed and performed as described below prior to their use in the functionalisation experiments.

All glassware was bought from Fisher scientific and VWR international. Prior to, and after every time using, glassware need to be carefully washed by a standard base bath followed by acid bath and thorough rinsing with MilliQ water to
avoid contamination. The base bath was made of 300 g of potassium hydroxide, 10 L of Isopropanol and 100 mL of Toluene and the acid bath was made of diluted hydrochloric acid. Glassware was immersed in the base bath for 24 hours at room temperature and then rinsed several times with MilliQ water. After the base bath wash, glassware were soaking in acid bath for 24 hours at room temperature and then followed by several times of MilliQ water wash. Afterwards, all glassware was dried at 60 °C or in the >100 °C oven.

All gas cylinders introduced in this project were at highest available purity and supplied by BOC.

7.1.2 Mass spectrometry

Mass spectrometry data were obtained on a Bruker Daltonics electrospray ionisation – time-of-flight (ESI-TOF) mass spectrometry at University of Bath. All mass spectrometry samples were prepared by dissolving in methanol, acetonitrile or distilled water. For porphyrin molecule sample characterisation, a few drops of formic acid were introduced to the solution to obtain better ionisation. The concentration of measured samples should be in a range of 1 µg/mL to 10 µg/mL. Positive loop injection and negative loop injection are the two method used in the project. Mass spectrometry data can be further analysed by Bruker Daltonics Data Analysis 4.0 software.

7.1.3 Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker 300 Ultrashield™ (¹H: 300 MHz, ¹³C: 75.5 MHz) at the University of Bath. NMR measurement methods were applied in this project includes: ¹H, ¹³C, COSY, HSQC and HMBC. All chemical compounds sample measured by NMR were dissolved in chloroform-d, methanol-d or dimethyl-d₆ sulfoxide. Chemical shifts (σ) of NMR spectra were recorded in parts per million (ppm) and relative signal, which
is normally tetramethylsilane (TMS), as an internal standard. The multiplicity and general assignments of the spectroscopic data were presented as: singlet (s), doublet (d), triplet(t), quartet (q), doublet of doublet (dd), doublet of doublet of doublet (ddd), doublet of triplet (dt) triplet of triplet (tt), unresolved multiplet (m), apparent (app), broad (br) and aromatic (Ar).

### 7.1.4 Raman spectroscopy

Raman spectroscopy was carried out on a Renishaw inVia Raman spectroscopy at Science & Technology Facilities Council (STFC), Central Laser Facility (CLF) or at the University of Bath. The measured samples used in this project normally contained carbon nanotubes, graphene oxide or reduce graphene oxide. The specimens were either in solid state or dispersed in pure water (MilliQ) or water: ethanol 1:1 mixture. During the measurement, the carbon nanomaterials samples were deposited on an aluminium plate substrate. (For some cases, silica wafer and glasses lens can also be used as the substrate, which specified in previous chapter when the case applied.) The input wavelength was set at 830 nm for single walled carbon nanotubes and their composite samples; and at 514 nm for graphene oxide, reduced graphene oxide and their composite samples. More than 10 times accumulations were generally applied in Raman spectroscopy measurements, and the beam was focussed in at least there different position across the specimen and these spectra were averaged to obtain batch-representative peaks and most reliable results.

### 7.1.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used in this project to measure the mass of a sample as a function of temperature or time. The TGA measurement was carried out on a Polymer Laboratories STA 1500 Simultaneous Thermogravimetric Analysis System. The sample applied in TGA measurement should be in solid state and approximately 5 mg of homogeneous sample was placed in a ceramic carrier,
crucible, which was then heated from room temperature up to 900°C at a rate of 2 °C per minute, with data points collected every 2 seconds. The TGA data collection was carried out under the direct supervision and with the help of Mr. Edward Aldred at University of Bath.

### 7.1.6 Hydrothermal synthesis

For the hydrothermal synthesis section of this project, special hydrothermal vessels (or autoclaves) are used to carry out the conversions at high pressure and high temperatures. The stainless steel autoclave design used was a Parr acid digestion bomb manufactured by the Parr Instrument Company. The reaction vessel contains an internal volume of 23 mL removable Teflon liner and possesses a maximum operating temperature and pressure of 250 °C and 1800 psi. After each reaction, the Teflon liner was washed several times with ethanol followed by cleaning using a sonication bath. This was necessary in order to remove the graphene sheets built-up attached on the walls of the Teflon liners. The hydrothermal synthesis was carried out under the direct supervision and with the help of Dr Qianlong Wang at the University of Bath.

### 7.1.7 Thin layer chromatography (TLC)

In this project, a commercially available Macherey-Nagel aluminium backed plates coated with a 0.20 mm layer of silica gel 60 Å with fluorescent indicator UV254 was introduced to TLC measurement. These plates were visualised by using either ultraviolet light with wavelength at 254 nm or 365 nm, or by staining the plates with vanillin or ninhydrin solution.

### 7.1.8 Silica gel column chromatography

Silica gel column chromatography was carried out by using Fisher or Sigma-Aldrich produced silica gel 60 Å (35-70 μm particle size). The solvent or
solvent combination applied in column chromatography depends on the polarity of different samples.

### 7.1.9 Fluorescence spectroscopy

Fluorescence spectroscopy measurement was carried out on a Perkin Elmer Luminescence spectrophotometer LS 55 at the University of Bath. All solvents used in fluorescence measurement were of a HPLC grade. MilliQ water was used for those experiments carried out in aqueous media. A 1.2 mL volume quartz cuvette with 10 mm path length was used as sample currier. The concentration of sample applied to fluorescence spectroscopy can vary between $10^{-5}$-10$^{-7}$ M depend on the strength of the fluorescence. A pre-scan (in the range between 200-900 nm) was recommended to determine the maximum excitation and emission wavelength. FL WinLab v1.60 is the software used to collect and further analysis data.

### 7.1.10 Ultraviolet–visible spectroscopy (UV-vis spectroscopy)

UV-vis spectroscopy was carried out by using a Perkin-Elmer Lambada 35 spectrometer and two quartz cuvettes (one for standard solvent, the other one for measuring sample). HPLC grade solvents and distilled water were applied in the measurement. A calibration process was performed before each measurement.

### 7.1.11 Transmission electron microscope (TEM)

Transmission electron microscope (TEM) images were obtained with Gatan Dualvison digital camera on a JEOL 1200EXII transmission electron microscope coupled with Energy-dispersive X-ray spectroscopy (point resolution, 0.16 nm) at the Physics Department, University of Bath. The operating voltage is 20 kV. High resolution transmission electron microscope (HRTEM) images were obtained on a Transmission Electron Microscope (TEM): JEM-2100 LaB6 at Research Complex at Harwell. TEM/HRTEM grid used in this PhD project is a Lacey carbon
film-Copper grid, purchased from Agar Scientific.

### 7.1.12 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6480LV scanning electron microscope or JEOL JSM-6301F scanning electron microscope. The JSM6480LV SEM machine coupled with an Oxford INCA X-ray analyser, which can be used for mapping, scanning and quantitative analysis, while, the JSM-6310F can obtain higher resolution images compared with JSM-6480LV but no elements analysis. Since almost all samples applied in SEM measurement in this project were carbon nanomaterials, Highly Ordered Pyrolytic Graphite (HOPG) was introduced as the sample substrate rather than direct deposited on an aluminium substrate or double coated conductive carbon tapes.

For the hydrothermal method when a 3 dimensional carbon nanohybrid sample was prepared, prior to imaging a pre-freeze dry progress was introduced in the sample preparation to hold the fragile 3D structure undisturbed. All prepared samples were kept in a desiccated environment overnight prior the observation.

### 7.1.13 Atomic Force Microscopy (AFM)

The Atomic Force Microscopy measurement was carried out a Digital Instruments Multimode Atomic Force Microscope with IIIa controller at Oxford University by Dr Robert Jacobs or Dr John Mitchels at University of Bath.

All AFM measurement presented in this project were obtained under tapping mode and the measuring probes are Silicon Probes (Nascatec GmbH model NST-NCHFR). The AFM samples were deposited onto freshly cleared mica substrate by spin coating (Laurell Technologies WS-400, 3000rpm) or HOPG substrate depends on the sample dispersibility and hydrophilicity.
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7.1.14 Fourier transform Infrared spectra (FTIR)

Fourier transform Infrared spectra were obtained by using a Perkin-Elmer 1000 FT-IR spectrometer at University of Bath. Characteristic absorption peaks are reported in wavelength (cm\(^{-1}\)).

7.1.15 Ultra-sonication

The Ultra sonication was carried out by using U-500 30 kHz sonication bath or Agar Scientific S0080 Sonomatic 30 kHz, 80 W sonication bath at room temperature. In this project, the sonication treatments were normally used to disperse carbon nanomaterials in organic solvent or distilled water, in order to avoid long time causing damage to the structure of carbon nanomaterials, it was carefully observed that no longer than 15 min sonication treatment was performed at once.

7.1.16 Density Functional Theory DFT calculation

All calculations were performed using density functional theory (DFT) as employed in Gaussian09, using B3LYP 6-31G(d,p).\(^4\,^5\) This was carried out via the High Performance Computing Facility, Aquila, University of Bath under the direct supervision and with the help of Dr Rory Arrowsmith.

7.1.17 Fluorescence lifetime measurements

Fluorescence lifetime measurements using single-photon excitation experiments were performed at the Rutherford Appleton Laboratory under the supervision of Prof S Botchway (Central Lasers facility, Research Complex at Harwell). An optical parametric oscillator was pumped by a mode locked Mira titanium sapphire laser (Coherent Lasers Ltd), generating 180 fs pulses at 75 MHz and emitting light at a wavelength of 580-630nm nm. The laser was pumped by a solid state continuous wave 532 nm laser (Verdi V18, Coherent Laser Ltd), with the
oscillator fundamental output of 473 ± 2 nm or 405 ± 2 nm. The laser beam was focused to a diffraction limited spot through a water immersion ultraviolet corrected objective (Nikon VC x60, NA1.2) and specimens illuminated at the microscope stage of a modified Nikon TE2000-U with UV transmitting optics. The focused laser spot was raster scanned using an XY galvanometer (GSI Lumonics). Fluorescence emission was collected without de-scanning, bypassing the scanning system and passed through a coloured glass (BG39) filter. The scan was operated in normal mode and line, frame and pixel clock signals were generated and synchronised with an external fast microchannel plate photomultiplier tube used as the detector (R3809-U, Hamamatsu, Japan). These were linked via a Time-Correlated Single Photon Counting (TCSPC) PModule SPC830. Lifetime calculations were obtained using SPCImage analysis software (Becker and Hickl, Germany) or Edinburgh Instruments F900 TCSPC analysis software.

7.1.18 Cyclic voltammetry measurements

For cyclic voltammetry studies, a microAutolab II potentiostat system (EcoChemie, Netherlands) was employed with a KCl-saturated calomel reference electrode (SCE, Radiometer). The measurements were carried out by using working electrode: 4.9 mm diameter basal-plane pyrolytic graphite (bppg) electrode, counter electrode: platinum wire, reference electrode: platinum wire with Ferrocene/Ferrocene⁺ solution as the standard, in a 0.1 M tert-butyl perchlorate in acetonitrile as the electrolyte; or using working electrode: 4.9 mm diameter basal-plane pyrolytic graphite (bppg) electrode, counter electrode: platinum wire, reference electrode: Calomel electrode, calomel in 0.1 M NaClO₄.
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7.2 Starting materials

The originally reported synthesis, dating from 1959 by A.W. Johnson and L. T. Kay was not reproducible, despite numerous repeats and attempts and trials by several members of the group, including Dr Sofia Pascu. Therefore each of the reaction steps needed to be adapted and the resulting products fully characterised.

7.2.1 3-Hexylpentane-2,4-dione (1)

For compound 1, 21.2 g (14.75 mL) of 1-iodohexane, 10.0 g (10.42 mL) of pentane-2,4-dione and 13.8 g of potassium carbonate were added into a 200 ml round bottom flask. In this reaction, the starting materials were mixed in a 1:1:1 ratio at 100mmol. Afterward, 50 mL dry DMF was added into the round bottom flask. The mixture was then refluxed at 100 °C overnight under nitrogen protection for. The mixture is left to cool down to room temperature after reflux. The DMF and pentane-2,4-dione were then removed under vacuum in the Schlenk line. After DMF and pentane-2,4-dione were fully removed, the remaining potassium carbonate (solid) was then removed by filtration and followed by washing several times with acetone. Once the acetone was removed by evaporation, the resulting brown oil was separated by a fractional distillation. Remaining acetone was separated out as the first fraction, at 20°C; 1-iodohexane was removed as second fraction, at 60 °C; final product compound 1 was separated out as the third fraction as a clear oil, at 120 °C (9.39 g, yield: 51.0%).
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\( ^1\text{H NMR} \) (300MHz, CDCl\(_3\), 25°C): \( \delta \) 3.66-3.55 (m, 1H, H-C(2)), 2.15 (s, 6H, H-C(1), H-C(3)), 1.86-1.74 (m, 2H, C-H(4)), 1.43-1.14 (m, 8H, H-C(5), H-C(6), H-C(7), H-C(8)), 0.92-0.82 (t, 3H, H-C(9), J=8.1 Hz).

\( ^{13}\text{C NMR} \) (75.5 MHz, CDCl\(_3\), 25°C): \( \delta \) 204.6 (\( \times 2 \), C(10)), 69.09 (C(2)), 31.48 (C(4)), 29.52 (C(5)), 29.05 (C(3)), 28.37 (C(6)), 27.52 (C(7)), 22.54 (C(8)), 14.02 (C(9)).

**Mass spectrum** ESI-MS calculated for C\(_{11}\)H\(_{21}\)O\(_2^+\) [M+H]\(^+\) 181.15, found 181.1569.

### 7.2.2 2-Benzyl-2-hydroxyimino-3-oxobutanoate (2)

![Chemical structure of 2-Benzyl-2-hydroxyimino-3-oxobutanoate](image)

For compound 2, 2.17 g benzyl acetoacetate (192.21 g/mol, 0.011mol) was added to 5 mL of acetic acid in a round bottom flask with a side arm. This round bottom flask was then placed into a salt/ice bath and allowed to cool down while stirring. 0.94 g sodium nitrite was dissolved into 2 mL water, and this solution was added dropwise to the stirring benzyl acetoacetate solution by a dropping funnel. During this process, some yellow precipitate may form, which was further dissolved with a few drops of acetic acid. After all the sodium nitrite solution was added, the mixture was allowed to cool down to the room temperature and left stirring overnight. The product compound 2 was extracted by using diethyl ether and washed several times with water to remove the acetic acid. The organic portion was dried with magnesium sulphate and the solvent removed to afford an orange oil (2.117 g, yield: 87%)

\( ^1\text{H NMR} \) (300MHz, CDCl\(_3\), 25°C): \( \delta \) 10.01 (s, 1H, H-O), 7.31-7.22 (m, 5H, H-C(6-11)), 5.26 (s, 2H, H-C(5)), 2.30 (s, 3H, H-C(1))

\( ^{13}\text{C NMR} \) (75.5 MHz, CDCl\(_3\), 25°C): \( \delta \) 194.00 (C(2)), 161.67 (C(4)), 150.43 (C(3)),

254
134.58 (C(6)), 128.64 (×2, C(8), C(10)), 128.61 (C(9)), 128.32 (×2, C(7), C(11)),
67.83 (C(5)), 25.36 (C(1))

Mass spectrum ESI-MS calculated for C₁₁H₁₂NO₄⁺ [M+H]^+ 222.07, found 222.0745.

7.2.3 Benzyll-4-(n-hexyl)-3,5-dimethylpyrrole (3)

For compound 3, a solution of 25 mL 3-hexylpentane-2,4-dione (9.2 g, 50 mmol) in acetic acid was stirred in a three neck round bottom flask. A solution of benzyl-2-hydroxyimino-3-oxotutanoate (11.1 g, 50 mmol) in 20 mL mixture of acetic acid and water (at a ratio of 3:1) was added dropwise, over a 20 minute period. During this time, 13.1 g, 200 mmol zinc dust was added into the solution in small portions. The reaction was then heated to 100 °C and stirring for overnight. Afterward, 50 g ice was directly added into the solution to quench the reaction. Then the products were separated by an extraction (performed using chloroform) and washed several times with water. The organic phase was collected after all solvent was removed. The product was then completely dried under vacuum, which allowed to remove any remaining acetic acid. Compound 3 was recrystallised from methanol under -18 °C. The final product was then washed with cold methanol and dried under vacuum to afford a white powdery solid (3.6 g, yield: 23%).

¹H NMR (300MHz, CDCl₃, 25°C): δ 8.49 (s, 1H, H-N), 7.38-7.52 (m, 5H, H-C(15-20)), 5.21 (s, 2H, H-C(14)), 2.26 (t, 3H, H-C(6), J=7.0Hz), 2.20 (s, 3H, H-C(11)), 2.10 (s, 3H, H-C(9)), 1.40-1.51 (m, 8H, H-C(2), H-C(3), H-C(4), H-C(5)), 0.80 (t, 3H, H-C(1), J=6.9 Hz).
13C NMR (75.5 MHz, CDCl₃, 25°C): δ 136.72(C(10)), 136.32(C(15)), 129.80(C(8)), 128.54×2(C(17), C(19)), 128.11×2(C(16), C(20)), 128.02(C(18)), 122.64(C(7)), 116.30(C(12)), 65.38(C(14)), 31.80(C(4)), 30.84(C(5)), 29.17(C(3)), 24.04(C(6)), 22.71(C(2)), 14.14(C(1)), 11.59(C(11)), 10.74(C(9)).

Mass spectrum ESI-MS calculated for C₂₀H₂₆NO₂⁻ [M-H]⁻ 313.20, found 313.1964.

7.2.4 Benzyl-5-acetoxyethyl-4-(n-hexyl)-3,5-dimethyl pyrrole (4)

For compound 4, 5.5 g lead (IV) acetate (12.48 mmol) was added in small portions to a stirring 40 mL acetic acid solution of compound 3 (3.9 g, 12.48 mmol). Then, the reaction was allowed to continue stirring until all the starting materials had been reacted, which was monitored by TLC (2:8 ethyl acetate : hexane). This process took approximately 3 hours. The solvent was then removed under vacuum. The remaining mixture was re-dissolved in 100 mL chloroform and then filtered to remove the undissolved lead acetate. Afterwards, the remaining organic phase was washed several times with water and dried over magnesium sulphate. The remaining solvent was then removed to afford an orange solid. This orange solid was recrystallised from methanol under -18 °C and dried under vacuum to afford compound 4 as a white powdery solid. (813 mg, yield: 17%).

1H NMR (300MHz, CDCl₃, 25°C): δ 8.93 (s, 1H, H-N), 7.38-7.22 (m, 5H, H-C(17-22)), 5.24 (s, 2H, H-C(16)), 4.93 (s, 2H, H-C(9)), 2.63 (t, 2H, H-C(6), J=7.43 Hz), 2.21 (s, 3H, H-C(11)), 1.99 (s, 3H, H-C(12)), 1.17-1.23 (m, 8H, H-C(5), H-C(4), H-C(3), H-C(2)), 0.8 (t, 3H, H-C(1), J=6.9 Hz).
\[^{13}\text{C NMR}\] (75.5 MHz, CDCl\(_3\), 25°C): \(\delta\) 171.60 (C(10)), 161.16 (C(15)), 136.39 (C(17)), 128.57 (\times 2, C(18), C(22)), 128.18 (\times 2, C(19), C(21)), 128.14 (C(20)), 127.16 (C(13)), 121.80 (C(7)), 65.71 (C(9)), 57.04 (C(16)), 31.75 (C(3)), 31.30 (C(4)), 29.11 (C(5)), 23.36 (C(6)), 22.67 (C(2)), 20.96 (C(11)), 14.11 (C(1)), 10.52 (C(12)).

**Mass spectrum** ESI-MS calculated for C\(_{22}\)H\(_{29}\)NNaO\(_4\)\([\text{M+Na}]^+\) 394.21, found 394.20.

### 7.2.5 5,5'-Dibenzyl-3-3'-di-(n-hexyl)-4,4'-dimethyldipyromethane (5)

![Chemical structure of 5](image)

For compound 5, 400 \(\mu\)L concentrated HCl were added to a warm methanol solution of 2 g of compound 3 in 20 mL, and then the mixture was allowed to reflux under nitrogen for approximately 5 hours, until the solution had become dark orange and the starting materials consumed, which was monitored by TLC. After cooling down to room temperature, 20 mL water was added and the solution extracted twice with 20 mL dichloromethane. The combined organic extracts were washed with saturated 20 mL Na\(_2\)CO\(_3\) solution and 20 mL water, then dried over Na\(_2\)SO\(_4\) and filtered. The solvent was removed to leave a crude red gum, which was recrystallised from cold methanol to afford compound 5 as peach coloured crystals. (280 mg, yield: 14%).

\[^1\text{H NMR}\] (300MHz, CDCl\(_3\), 25°C): \(\delta\) 8.54 (s, 2H, H-N(1), H-N), 7.21-7.32 (m, 10H,
H-C(15-20), 5.18 (s, 4H, H-C(14)), 3.74 (s, 2H, H-C(3)), 2.27 (t, 4H, H-C(4), J=7.4Hz), 2.20 (s, 6H, H-C(5)), 1.14-1.32 (m, 16H, H-C(6), H-C(7), H-C(8), H-C(9)), 0.79 (t, 6H, H-C(10), J=6.90Hz).

$^{13}$C NMR (75.5 MHz, CDCl$_3$, 25°C): δ 136.43 (×2, C(15)), 128.50 (×4, C(18), C(20)), 128.00 (×2, C(18)), 127.93 (×4, C(17), C(19)), 127.74 (×2, C(11)), 123.05 (×2, C(1)), 117.54 (×2, C(12)), 65.60 (×2, C(14)), 31.76 (×2, C(6)), 30.97 (×2, C(7)), 29.31 (×2, C(8)), 24.12 (×2, C(4)), 23.24 (C(3)), 22.18 (×2, C(9)), 14.13 (×2, C(10)), 10.80 (×2, C(5)).

Mass spectrum ESI-MS calculated for C$_{39}$H$_{50}$N$_2$NaO$_4$ $^{+}$[M+Na]$^+$ 633.83, found 633.79.

7.2.6 α-Bromo-m-tolylaldehyde (8)

For compound 8, 1 g α-Bromo-m-tolunitrile (5.1 mmol) was dissolved in 40 ml of toluene and cooled to 0 °C by ice bath under nitrogen. Diisobutylaluminiumhydride (DIBAL-H, 1.0 M in hexanes, 7 mL, 7 mmol) was added dropwise, and the resulting solution stirred for an hour. The solution was then diluted with 40 mL CHCl$_3$, followed by another dilution with 200 mL concentrated HCl, and then the diluted solution stirred for 1 hour at room temperature. The organic layer was separated, and washed twice with 100 mL water. It was then dried over MgSO$_4$, filtered off, and the solution concentrated to a few millilitres. The solvent was then removed and then recrystallised from petroleum ether under -18 °C to afford white crystals (789 mg, yield: 78%).

$^1$H NMR (300MHz, CDCl$_3$, 25°C): δ 9.90 (s, 1H, H-C(1)), 7.83 (s, 1H, H-C(2)), 7.75 (d, 1H, H-C(3), J=6.3 Hz), 7.59 (d, 1H, H-C(4), J=7.63 Hz), 7.45 (t, 1H, H-C(5), J=7.63 Hz), 4.46 (s, 2H, H-C(6)).
\[^{13}\text{C} \text{NMR}\ (75.5 \text{ MHz, CDCl}_3, 25^\circ\text{C}): \delta\ 192.72\ (\text{C}(1)), 137.90\ (\text{C}(7)), 136.56\ (\text{C}(8)), 135.14\ (\text{C}(5)), 130.01\ (\text{C}(4)), 129.33\ (\text{C}(3)), 128.43\ (\text{C}(2)), 32.69\ (\text{C}(6)).\]

Mass spectrum ESI-MS calculated for C\textsubscript{8}H\textsubscript{8}BrO\textsuperscript{+} [M+H]\textsuperscript{+} 199.05, found 200.01.

7.2.7 3-(S-Acetyliothiomethyl)benzaldehyde (9)

For compound 9, a solution of 780 mg \(\alpha\)-bromo-m-tolylaldehyde (3.9 mmol) in 20 mL acetone was added into 625 mg potassium thioacetate (5.4 mmol) with stirring. Afterward, the mixture was refluxed for 3.5 hours under nitrogen, until no starting material was visible by TLC. When the mixture was cooled down to room temperature, 40 mL water was added and extracted three times with 15 mL ethyl acetate. Then the solvent was removed. The product was purified by column chromatography (diethyl ether/hexane 1:1, dry loading) to give the compound 9 as a brown oil. (680 mg, yield: 87%).

\[^{1}\text{H} \text{NMR}\ (300\text{MHz, CDCl}_3, 25^\circ\text{C}): \delta\ 9.93\ (s, 1\text{H, H-C}(1)), 7.73\ (s, 1\text{H, H-C}(7)), 7.70\ (d, 1\text{H, H-C}(3), J=7.5\text{ Hz}), 7.51\ (d, 1\text{H, H-C}(5), J=6.2\text{ Hz}), 7.41\ (t, 1\text{H, H-C}(4), J=9.5\text{ Hz}), 4.10\ (s, 2\text{H, H-C}(8)), 2.33\ (s, 3\text{H, H-C}(10)).\]

\[^{13}\text{C} \text{NMR}\ (75.5 \text{ MHz, CDCl}_3, 25^\circ\text{C}): \delta\ 194.78\ (\text{C}(9)), 192.07\ (\text{C}(1)), 139.74\ (\text{C}(2)), 136.74\ (\text{C}(6)), 134.91\ (\text{C}(4)), 129.96\ (\text{C}(5)), 129.36\ (\text{C}(3)), 128.68\ (\text{C}(7)), 32.89\ (\text{C}(8)), 30.37(\text{C}(10)).\]
For synthesis of compound 10, 130 mg starting material compound 5 were dissolved into 20 mL THF (containing 0.2 mL Et$_3$N, 1%) in a three necked round bottom flask. After the mixture was then degased by nitrogen and vacuum, 50 mg palladium on carbon was added into this mixture. The black suspension was degassed again and then leaved under hydrogen for two hours at room temperature. After all starting materials have been consumed, monitored by TLC (hexane : ethyl acetate=1:1), the catalyst was filtered off though a plug of Celite. The filtrate was then concentrated to afford pink crude and further dried under vacuum. Cold, degassed TFA was added to this crude by cannula and the mixture was leaved stirring under $0^\circ$C for one hour. Afterwards, a degased methanol solution of compound 9 was added into the mixture by cannula and the mixture was left stirring under $-19^\circ$C (ice salt bath) for two and half hours. 180 mg 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added into the mixture and stirring continued overnight to make sure the oxide reaction fully happened. 20 mL triethylamine (Et$_3$N) was added dropwise and then the solvent removed by evaporation. The residue was then re-dissolved in 100 mL CH$_2$Cl$_2$ and then washed five times 75 mL water, and dried over sodium sulphate, filtrated and passed through a plug of silica gel. Column chromatography was then introduced to afford purified compound 10. Crystals suitable for X-ray diffraction were grown from a
saturated solution of porphyrin in CH$_2$Cl$_2$ layered with Methanol (15.6 mg, yield: 12%).

$^1$H NMR (500MHz, CDCl$_3$, 25°C): δ 10.26 (s, 2H, H-C(10)), 8.05 (s, 2H, H-C(18)), 7.98-7.93 (m, 2H, H-C(16)), 7.77-7.72 (m, 2H, H-C(14)), 7.69 (t, 2H, H-C(15), J=7.6 Hz), 4.43 (s, 4H, H-C(19)), 4.01 (t, 8H, H-C(22), H-C(28), J=7.9 Hz), 2.50 (s, 12H, H-C(11), H-C(12)), 2.42 (s, 6H, H-C(21)), 2.25-2.19 (m, 8H, H-C(23), H-C(29)), 1.80-1.74 (m, 8H, H-C(24), H-C(30)), 1.56-1.46 (m, 8H, H-C(25), H-C(31)), 1.44-1.36 (m, 8H, H-C(26), H-C(32)), 0.94 (t, 12H, H-C(27), H-C(33), J=7.3 Hz), -2.39 (s, 2H, H-N)

$^{13}$C NMR (75.5 MHz, CDCl$_3$, 25°C): δ 195.3 (C20), 145.0 (C17), 143.4(C13), 142.6(C5), 141.5(C4), 136.8(C3), 136.2(C2), 133.5 (C18), 132.0 (C16), 128.7 (C14), 127.9 (C15), 117.5 (C1), 97.1 (C10), 33.8 (C19), 33.3 (C23, C29), 32.0 (C25), 31.0 (C31), 30.4 (C21), 30.0 (C24), 26.8 (C22), 26.8 (C28), 22.8 (C26), 33.2), 14.8 (C11, C12), 14.2(C27), C(33));

Mass spectrum ESI-MS calculated for C$_{66}$H$_{87}$N$_4$O$_2$S$_2$ [M+H]$^+$ 1030.62, found 1031.63.
7.2.9 5,15-Di(3-acetylthiomethylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrinato zinc(II) (11)

![Chemical Structure]

Compound 11, was converted from free base porphyrin, compound 8, by treatment with excess Zn(OAc)$_2$$\cdot$H$_2$O. The excess of 10 mg Zn(OAc)$_2$$\cdot$H$_2$O was added to a solution of 4 mg compound 8 in 7 mL DMF and the mixture was then treated with microwave under 150°C for 10 minutes. After the reaction mixture was cooled to room temperature, the DMF removed under vacuum. The residue was re-dissolved in CHCl$_3$ and washed five times with water and brine and dried over sodium sulphate. The CHCl$_3$ was then removed under reduced pressure. Recrystallisation was carried out by using a combination (CHCl$_3$ : MeOH (9:1)/hexane) of solvents in layered fashion (3.32 mg, yield: 83%).

$^1$H NMR (500MHz, DMSO, 25°C): δ 10.05 (s, 2H, H-C(10)), 7.97 (s, 2H, H-C(18)), 7.91-7.85 (m, 2H, H-C(16)), 7.79-7.74 (m, 2H, H-C(14)), 7.74-7.69 (m 2H, H-C(15)), 4.42 (s, 4H, H-C(19)), 3.93 (t, 8H, H-C(22), H-C(28), J=7.7 Hz), 2.39 (s, 6H, H-C(21)), 2.36 (bs, 12H, H-C(11), H-C(12)), 2.17-2.06 (m, 8H, H-C(23), H-C(29)), 1.77-1.66 (m, 8H, H-C(24), H-C(30)), 1.54-1.43 (m, 8H, H-C(25), H-C(31)), 1.41-1.30 (m, 8H, H-C(26), H-C(32)), 0.89 (t, 12H, H-C(27), H-C(33), J=7.3 Hz)

$^{13}$C NMR (75.5 MHz, CDCl$_3$, 25°C): δ 195.3 (C(20)), 147.2 (C(17)), 146.0(C(13)), 144.7(C(5)), 144.1(C(4)), 143.4(C(3)), 134.2(C(2)), 133.8 (C(18)), 132.0 (C(16)), 130.8 (C(19)), 129.2 (C(15)), 128.8 (C(21)), 128.0 (C(14)), 127.7 (C(16)), 126.4 (C(18)), 124.6 (C(24)), 120.3 (C(12)), 117.1 (C(2)), 114.5 (C(3)), 110.3 (C(26)), 84.0 (C(29)), 38.8 (C(10)), 37.2 (C(22)), 34.9 (C(28)), 31.0 (C(19)), 29.4 (C(23)), 29.2 (C(25)), 26.5 (C(31)), 25.9 (C(24)), 24.7 (C(30)), 21.1 (C(21)), 19.6 (C(11)), 19.3 (C(12)), 18.0 (C(27)), 17.9 (C(33)), 17.7 (C(29)), 16.3 (C(26)), 16.2 (C(32)), 15.7 (C(28)), 15.6 (C(32)), 15.5 (C(29)).
97.3 (C(10)), 33.6 (C(19)), 33.2 (C(23), C(29)), 31.9 (C(25), C(31)), 30.8 (C(21)), 29.8 (C(24), C(30)), 26.5 (C(22), C(28)), 22.7 (C(26), C(32)), 15.4 (C(11), C(12)), 14.5 (C(27), C(33))

**Mass spectrum** ESI-MS calculated for C$_{66}$H$_{83}$N$_4$O$_2$S$_2$Zn$^-$ [M-H] 1091.53, found 1091.59.

### 7.2.10 5,15-Di(3-mercaptomethylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethyl-porphyrinato zinc(II) (12)

![Structure of compound 12](image)

Dr Amy Kieran has confirmed the dimer structure can be formed by exposing Zn(II)-porphyrin in air for a long time. The crystal structure of de-protected Zn(II)-porphyrin dimer, which obtained by Dr Sofia Pascu, is presented in appendix xii, figure D.1 and D.2. Alternatively, the de-protected monomer Zn(II)-porphyrin can also be generated by a de-protecting reaction: 3 mg Zn(II)-porphyrin compound 11 was dissolved in degassed 5 mL CH$_2$Cl$_2$, then 200 μL hydrazine monohydrate was added to this mixture. This solution was stirred under nitrogen for overnight and then the solvent was removed under reduced pressure. The left residue was re-dissolved in degassed 10 mL CH$_2$Cl$_2$ and washed twice with 20 mL degassed water under nitrogen. The organic phase was dried over sodium sulphate, and then the solvent was removed by reduced pressure to afford compound 10 (2.67 mg, 89%).
\textbf{Chapter 7 Experimental Section}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of the compound under study.}
\end{figure}

$^1\text{H NMR}$ (500MHz, CDCl$_3$, 25°C): 10.19 (s, s, 2H, H-C(10)), 8.06 (s, 2H, H-C(18)), 7.96 (m, 2H, H-C(16)), 7.70 (m, 2H, H-C(14)), 7.54 (t, 2H, H-C(15), J=7.6 Hz), 4.01 (s, 4H, H-C(19)), 3.96 (t, 8H, H-C(22), H-C(28), J=7.9 Hz), 2.48 (s, 12H, H-C(11), H-C(12)), 2.21-2.15 (m, 8H, H-C(11), H-C(12)) 1.96 (t, 2H, H-S), 1.75 (m, 8H, H-C(24), H-C(30)), 1.39 (m, 8H, H-C(25), H-C(31)), 1.31 (m, 8H, H-C(26), H-C(32)), 0.94-0.87 (t, 12H, H-C(27), H-C(33));

\textbf{Mass spectrum} ESI-MS calculated for C$_{62}$H$_{80}$N$_{4}$S$_{2}$ZnNa$^+$ [M+Na]$^+$ 1031.51, found 1031.62.

\section*{7.3 Purification and functionalisation of single walled carbon nanotubes}

\subsection*{7.3.1 Acid wash purified single walled carbon nanotubes}

A schematic representation of the impurities which may be found on the surface of carbon nanotubes is shown below. This method was adapted from an earlier published method.\textsuperscript{6}
The acid wash-based purification method applied in this project to all SWNTs used included the steps described as follows. Firstly, the whole purification process started with a microwave heating step, to expose metal catalyst encapsulated within carbon nanoparticles. Secondly, a sonication process was introduced to disperse those aggregated SWNTs. Next, a hydrochloric acid wash was followed by a microfiltration and a MilliQ water rinse aiming to dissolve and rinse the solubilised salts of the metal catalyst. Subsequently, an oxidative treatment using concentrated nitric acid was performed in order to oxidise the amorphous carbon and graphite carbon and finally, a NaOH/aqueous wash followed by filtration were carried out to enhance the solubility of the oxidised amorphous carbon and graphite carbon adherent to the pristine SWNTs tubes. This proved an invaluable step as it was necessary to wash all these impurities away from the surface of single-walled carbon nanotubes. This acid wash purified methods can be used to those single-walled carbon nanotubes which contain lots of metal nanoparticles catalysts (typically Ni, Fe, Y, Mo) as well as amorphous carbon sheets.

In a typical acid wash purification experiment, 20 mg of as-made arc-synthesised single-walled carbon nanotubes (Carbolex, Rice) were weighed out in fume cupboard and the operator should wear a facial mask. Afterward, the single-walled carbon nanotubes were added into 20 mL H₂O₂ aqueous solution (30%) in 50 mL centrifuge tube. The suspension was then treated with 30 min sonication (Ultrawave U-500 30 Hz or Agar scientific S0080 Sonomatic 30 Hz, 80W) to make sure most single-walled nanotubes can be dispersed in H₂O₂. As a prolonged sonication may cause damages to the surface of the SWNTs, the 30 min sonication progress necessary for dispersion was separated into 3 times 10 min sonication treatment within 5 min intervals. Then, the suspension was separately added into four 10 mL microwave vials for microwave heating treatment (Biotage initiator 2.0). The microwave treatment was carried out at 120 W and 40 °C for 2
min and repeated five times. After microwave treatment, all the mixtures were collected in 50 mL centrifuge tubes and diluted with excess distilled water. The mixtures were then filtered by a nano-filtrate system by utilising a cyclopore track etched membrane. This was a hydrophilic membrane with 0.2 μm pores with resistance to inorganic corrosive aqueous solutions. The SWNTs samples left on the membrane were then collected and re-dispersed into 40 mL of 16% conc. hydrochloric acid. The mixture was then refluxed at 120 °C with stirring for 12 hours. After that, the mixture was diluted with excess distilled water and neutralized with NaOH and subsequently filtered through a cyclopore track etched membrane. The solids on the filtrate membrane were collected and re-dispersed into 25 mL distilled water, and then 15 mL 9 M HNO₃ was added into this solution. The mixture was refluxed at 100 °C for 24 hours. Afterwards, the mixture was filtered and the solids on the membrane were rinsed with excess distilled water. The SWNTs were re-dispersed into 20 mL distilled water with of 5 min sonication. In the last step, 100 mL of 8M NaOH was added to the mixture. The solution was then refluxed whilst stirring for 48 hours in a special designed PMP (Polymethylpentene) container, which contained a nitrogen inlet and an exhaust for excess pressure to protect the single-walled nanotubes. Afterwards, this mixture was diluted with 1 L distilled water and then filtered by a nano-filtration system. The SWNTs on the membrane were collected and further rinsed with 500 mL distilled water. This washing process was repeated 3 times to make sure all the NaOH was removed. The SWNTs were then washed with excess toluene to remove carbonaceous materials stuck to the outer tubes surface. The purified single-walled carbon nanotubes were then collected and stored in a 30mL glass vial and dried over 60 °C in a furnace overnight. Characterisation was carried out via TEM / SEM and Raman spectroscopy and representative images of the batches emerging are given in Chapter 2 and in Appendices.
7.3.2 Annealing step towards repairing the aromatic network of single-walled carbon nanotubes

A high temperature annealing progress was introduced hereby based on a previously reported method which was found to be efficient in order to repair single-walled carbon nanotubes surface defects.\(^7\)

In a typical experiment, single-walled carbon nanotubes used hereby were first stored inside a gloves box and purged with argon for one week to fully remove the oxygen molecules absorbed onto the surface. We found this was more effective than the use of a Schlenk line as the exposure to toxic SWNTs was reduced and the loss of airborne SWNTs particulate minimised. Afterwards, 10 mg of SWNTs powders were transferred inside a special designed quartz tube, 9 mm diameter and immobilised with quartz wool at both sides. The quartz tube was then placed into a furnace capable of high temperature heating. The furnace was purged under argon for 2 hours before heating. The increase rate of the temperature was set at 10 °C/min and the furnace was heated up to 1050 °C holding at this temperature for 2 hours. The whole annealing progress was purged by hydrogen and argon gas (1 : 9), in which molecular hydrogen was used as the reductive agent. After the furnace was cooled down to the room temperature, the sample was then collected, stored under Argon and deemed ready for further experiments and characterisation/imaging.
7.3.3  Steam purified single walled carbon nanotubes

This method was largely based on the method developed by the Oxford nanotube group.\textsuperscript{2,3}

In our hands, it was found that for an advanced purity sample to become available, the Elicarb tubes needed to be further purified in house, despite some initial purification by this method being performed at the Thomas Swan end prior to sample delivery.

In a typical steam purification reaction, 250 mg single-walled carbon nanotubes were kept in a glove box purged with argon for one week to fully removed oxygen absorbing on their surface. Afterward, the SWNTs were transferred to a special designed quartz tube, 9 mm diameter and immobilised with quartz wool at both side. Subsequently, the quartz tube was placed into a furnace capable of high temperature heating. The steam was introduced into the system by bubbling argon though boiling distilled water (98 °C) and the furnace was purged under argon for 2 hours before heating.\textsuperscript{3} The furnace was then gradually heated up by setting the increase rate of the temperature at 10 °C/min and the furnace was heated up to 1050 °C, kept at this temperature for 2 hours. Turn off the bubbled steam and kept purging argon into the system before the furnace was cooled down to room
temperature. The sample was then collected. Following the steam purification step, a further solution wash using aq. HCl (conc. 16%) was introduced. SWNTs were added into HCl and the mixture was stirring for overnight. The SWNTs sample was then filtrated and washed with excess distilled water; the solid phase was collected and dried over night at 60 °C.

7.3.4 Synthesis of non-covalently linked compound 11@SWNTs complex

A sample of purified single-walled carbon nanotubes (5 mg) was dispersed into 30 mL of ethanol. The mixture was treated with 3 times 10 min sonication, which had 5 min intervals, to make sure most of the purified SWNTs were dispersed in the solution. Then, the suspension was added into a 50 mL centrifuge tubes and treated with 30 min centrifugation at 3500 rpm. The top layer supernatant in the centrifuge tubes were carefully separated and collected to afford a SWNTs ethanol solution. Afterwards, 1 mg Zn(II)-porphyrin was added into 30 mL of chloroform and then the solution was added into the SWNTs solution. The mixture was then left
stirring for 12 hours at room temperature. Then, the mixture was filtrated and the solids on the membrane were rinsed with excess chloroform. The solid residue was then collected and fully dried over 60 °C. The final product (compound 11@SWNTs complex) was ready for further experiments and characterisation by spectroscopy/microscopy methods.

### 7.3.5 Bingel reaction functionalised single-walled carbon nanotubes

In a typical reaction, 30 mg of purified and annealed single-walled carbon nanotubes were weighted out and added to a quartz tube (Note: Facial mask, rubber gloves and goggles were required during weighting progress in air). Prior to the use of the single-wall carbon nanotubes in a Bingel reaction functionalised progress, an annealing surface preparation step was found imperative in order to repair any possible surface defects. The single-wall carbon nanotubes were thus first annealed by using a furnace under vacuum at $10^{-3}$ mbar and at 1000 °C for 3 hours under an atmosphere of N$_2$ for protection against combustion / rapid oxidation. Post-annealing, a Raman spectroscopy test was carried out and the repaired single-wall carbon nanotubes were then added into 15 mL dry ortho-dichlorobenzene (o-DCB) to obtain a suspension. A 15 min ultrasonic treatment in 80 w sonication bath was introduced to disperse the SWNTs. Afterwards, 1.8 mmol of diethyl bromomalonate and 3.3 mmol of
1,8-diazabicyclo[5.4.0]undecene (DBU) were added into carbon nanotube suspension and the mixture was left stirring for 15 hours under nitrogen protection at room temperature, followed by adding 3.9 mmol trifluoroacetic acid to quench the reaction.\(^8\) 35 mL ethanol was added into the mixture and then the mixture was transferred to a 50 mL centrifuge tube. A centrifugation progress, 3500 rpm and 30 min was introduced to separate the single-walled carbon nanotubes and thus facilitate the removal of the solvent. The washing of the SWNTs several times (using a special microfiltration apparatus) with ethanol was performed followed by the repeat of this centrifugation progress. The SWNTs was then collected by a microfiltration system and rinsed with more excess ethanol to fully remove the organic phase. The sample was then dried at 60 °C overnight. The final products were ready to be characterised by TEM and Raman spectroscopy.

**7.3.6 Synthesis of a covalently linked de-protected compound 11@SWNTs complex**

A bath of functionalised SWNTs using the Bingel reaction (synthesised as described in paragraph 6.3.5) were first synthesised. Next, these were transesterified
by prolonged stirring in an extensive of 2-mercaptoethanol (5 mL) for 72 hours under a protective atmosphere of nitrogen. Afterwards, the resulting product, denoted [(COOCH\(_2\)SH)\(_2\)C]-tagged SWNTs, was washed extensively with diethyl ether (80 ml). Then, the mixture was separated by microfiltration and the solid parts gathered onto the filtrate membrane were collected into a glass vial.

In parallel, the thiol-functionalised, de-protected porphyrins were synthesised following the method described in paragraph 6.2.10. A 1 mg sample of the transesterified single-walled carbon nanotubes was added as a solid to a 5 mM chloroform solution of de-protected porphyrin and then 0.2% equal 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was added into the mixture in a dropwise manner. The solution was stirred for 72 hours at room temperature. Afterwards, the mixture was filtrated and the solids on the membrane were rinsed with excess ethanol. The complex was then collected and transferred into a 30mL glass vial. The resulting materials (denoted de-protected compound 11@SWNTs complex) were then fully dried over 60 °C for overnight. The final products were then ready for further experiments and characterisations.

7.4 Synthesis and modification of graphene oxide/graphene and their porphyrin complex

7.4.1 Synthesis of graphene oxide

![Graphene Oxide (3D)](image)

![Graphene Oxide (2D)](image)
The method of synthesising graphene oxide applied in this project involved converting graphite powder into graphite oxide, and then forcing it separated into graphene sheets. The oxygen and carboxylic groups on or between the different layers of graphite oxide enlarge the inner distance between them, which made long time sonication possibly to easily exfoliate single layer or a few layers graphene oxide sheets out.

In a typical experiment, 10 g of powdered flake graphite and 5 g of sodium nitrate was stirred in 230 mL concentrated sulphuric acid a 1.5 L beaker and held at 0 °C on an ice bath. Whilst stirring, 30 g of potassium permanganate was added into the suspension and the adding rate was carefully controlled such that the temperature of the suspension did not exceed 20 °C. The beaker was then removed from the ice bath with stirring and the temperature was allowed back to room temperature. Afterwards, the mixture was left stirring for 30 min before 460 mL distilled water was slowly added into the mixture. This causes a rise in temperature and effervescence, and the mixture eventually turned from dark to brown. The mixture was then further diluted to approximately 1.4 L with distilled water. To reduce the excess manganese dioxide and to the soluble manganese sulfate, an aqueous solution of 3% H₂O₂ was added dropwise into the mixture, with stirring, until the mixture turned to bright yellow. The suspension was then filtrated whilst still warm, rinsed with excess warm distilled water. The solid was collected from the cyclopore membrane and re-dispersed in 3.2 L distilled water. The salt impurities were fully removed by treating with resinous anion and cation exchangers. Afterwards, the mixture was filtrated again and rinsed with distilled water. The solid fractions was collected and stored in a glass vial, followed by holding at 60 °C in a furnace overnight to make sure the graphite oxide was fully dried.

For the next step, 2 g of graphite oxide (synthesised as described above) were dispersed into 100 mL distilled water and ethanol (2:1) mixture followed by 3
hours sonication. Since prolonged sonication may cause damages to the aromatic network of carbon nanomaterials, the sonication period was separated into 6 times 30 min sonication sessions with 10 min interval between each session. Then, the mixture was separated into two 50 mL centrifuge tubes and each of them treated with 30 min centrifugation at 3500 rpm. The suspensions in the centrifuge tubes were separated to two phases, the graphene oxide dispersion layer on the top and unexploited graphite oxide powder depositing at the bottom. The graphene oxide dispersion was then carefully collected into a round bottom flask and treated with another dialysis progress for two weeks to fully remove remaining salt. Afterwards, the graphene oxide dispersion can apply to further experiment, for graphene oxide solid synthesis, the solvents were removed under reduced pressure by using a rota-evaporator, and the resulting solid residue was stored overnight at 60 °C to give the products fully dried, the final products were 1.4 g (yield was 70%).

7.4.2 High temperature Annealing reduce graphene oxide

In this research project, a high temperature annealing process was introduced to repair the surface defects by reducing the oxygen groups and carboxylic groups on the surface of the graphene oxide. In a typical experiment, 10 mg of graphene oxide powders were transferred inside a special designed quartz tube, 9 mm diameter and immobilised with quartz wool at both side. Afterwards, the quartz tube was placed into a furnace capable of high temperature heating. The furnace was purged under argon for 2 hours before heating. The increase rate of the temperature was set at 10 °C/min and the furnace was heated up to 1050 °C, kept at this temperature for 2 hours. The whole annealing progress was purged by hydrogen and
argon gas (1 : 9) and molecular hydrogen was used as a reductive agent. After the furnace was cooled down to room temperature, the sample was then collected (the final yield was 7.4g, 74%) and analysed by TEM, HRTEM and Raman spectroscopy.

### 7.4.3 Hydrothermally reduced graphene oxide

For a typical hydrothermal reduction reaction, 5 mg graphene oxide (obtained as described above) was dispersed in 10 mL ethanol. This dispersion was then added into a removable Teflon vessel which was then placed into the fitted stainless steel hydrothermal vessel (autoclaves). Afterwards, the autoclave was transferred into a furnace and held at 200 °C for 24 hours. Subsequently the autoclave was allowed to cool down to room temperature and it was found that the reduced graphene oxide turned into a black cylinder structure lining the walls of the Teflon vessel, which was then collected and analysed by TEM, HRTEM and Raman spectroscopy.

### 7.4.4 Ammonia and hydrazine hydrate reducing of graphene oxide

![Chemical reaction diagram]

The clear and stable graphene oxide solution (water and ethanol at ratio of 2:1 mixture) emerging from the process described above (Section 7.4.1) was introduced into a microfiltration apparatus and the graphene oxide solid was collected from the membrane filter (hole size 0.4 μm). Next, 5 mg of this graphene oxides material were suspended into 50 mL of distilled water. The suspension was then sonicated (3 times 10 min sonication, using U-500 30 kHz sonication bath) which has 5 min intervals between each section, to make sure that the graphene
oxides were fully dispersed without damaging the aromatic sheets. Then, the suspension was added into a 50 mL centrifuge tubes and treated with 30 min centrifugation at 3500 rpm. The top layer supernatant in the centrifuge tubes were carefully separated and collected to afford graphene oxide water solution. The chemical reduction method was then carried out by added 20 mL graphene oxide water solution, 7μL of hydrazine hydrate and 130μL of ammonia solution into a round bottom flask, the mixture was refluxed at 100 °C for 2 hours with constant stirring. The graphene oxide yellow solution turned to black suspension after chemical reduction. The solid in the suspension was then collected by filtration washing with excess distilled water to remove remaining salt and dried over 60 °C for overnight before further experiments and characterization by TEM, HRTEM and Raman spectroscopy. The yield was 75%.

7.4.5 Chemically and microwave-base reduced graphene oxide (rGO).

The chemically and microwave-based reduced graphene oxide was adjusted from an ammonia and hydrazine hydrate assisted reducing procedure, 10 mL graphene oxide water solution (0.5 mg/mL), 3μL of hydrazine hydrate and 75μL of ammonia solution were mixed, and then transferred into a microwave reaction carrier. The reaction was set at 100 °C and held for 15 min. The final products were then washed and collected by a nano-filtration system. After this products were fully dried (in oven at 60 °C, 12 hours), the products were then ready for further experiments and characterisations (Raman, TEM and HRTEM), the final yield was 4.3g, 86%.
7.4.6 Synthesis of non-covalently compound 11@GO

A clear and stable graphene oxide dispersion was formed using 2.5 g GO (emerging from the process described above in section 7.4.1) and a mixture of water and ethanol at ratio of 2:1 mixture, 5 mL. This suspension was introduced into a microfiltration apparatus (using a membrane filter with 0.4 μm pores) and after the filtration, the residual graphene oxide solid was collected from the membrane filter. Next, 5 mg graphene oxide materials were suspended into 50 mL of ethanol. The mixture was then sonicated for 30 minutes (3 times 10 min sessions, with 5 min intervals between each session, to make sure that the graphene oxides were fully dispersed). Then, the resulting mixture was added into a 50 mL centrifuge tubes and treated with 30 min centrifugation at 3500 rpm. The top layers of the supernatant from each of the centrifuge tubes were carefully separated and collected.

In parallel, 1 mM -SOAc protected compound 11 starting material was dissolved into 50 mL of ethanol. Afterwards, the compound 11 solution was added into the graphene oxide supernatant. The mixture was stirred for 24 hours. Subsequently, the mixture was filtered and the solids on the membrane were rinsed with excess ethanol. Graphene oxides and compound 11 complex were then
collected from the membrane. The complex was fully dried by using a 60 °C furnace for 12 hours. The final solid products were then deemed ready to be characterised by spectroscopic methods (IR, Raman and UV) and microscopy (TEM and SEM).

7.4.7 Synthesis of hydrothermally reduced compound 13@rGO complex

In a typical experiment, 5 mL graphene oxide (0.5 mg/mL) ethanol solution was mixed with 5 mL 0.1 mM compound 13 chloroform solution. 5 min sonication treatment was introduced to get better dispersion. The mixture was then transferred into a removable Teflon liner and then the Teflon liner was put into the fitted stainless steel hydrothermal vessel (autoclave). The autoclave was transferred into a furnace and held at 200 °C for 24 hours. After the autoclaves cooled down to room temperature, the rGO 3D nanomaterial resulting from the hydrothermal process, and denoted compound 13@rGO complex, was collected.

7.4.8 Synthesis hydrothermally reduced compound 14@rGO complex

The hydrothermally reduced compound 14@rGO complex was generated by a similar hydrothermal reaction analogous synthetic route that described above. A 5 mL graphene oxide ethanol dispersion (0.5 mg/mL) was mixed with a 5 mL 0.1 mM compound 14 chloroform solution. Then, a 5 min sonication treatment was applied to get ensure an optimum dispersion. The mixture was then transferred into a removable Teflon liner and this was then placed inside a stainless steel hydrothermal vessel (autoclave). The autoclave was then transferred into a furnace and held at 200 °C for 24 hours. After the autoclave cooled down to the room temperature, the rGO hydrogel complex was collected.
7.4.9 Synthesis of hydrothermally reduced compound 10@rGO complex

In a typical process, for the hydrothermal generation of compound 10@rGO complex, a 5 mL graphene oxide ethanol dispersion (0.5 mg/mL) were added to a 5 mL 0.1 mM compound 10 chloroform solution. A 5 min sonication treatment was introduced to get an optimum dispersed phase. The mixture was then transferred into a removable Teflon liner which was subsequently placed into a fitted stainless steel hydrothermal vessel (15 mL autoclave). The autoclaves were transferred into a furnace holding at 200 °C for 24 hours. After the autoclaves cooled down to room temperature, the rGO hydrogel complex and was collected.

7.5 Thermogravimetric analysis of porphyrins@rGO nanohybrids

Thermogravimetric analyses (TGA) of porphyrins@rGO and graphene oxide were applied in this project to measure the thermal stability by measuring mass of the complexes sample as a function of temperature or time. The TGA measurement was carried out on a Polymer Laboratories STA 1500 Simultaneous Thermogravimetric Analysis System at University of Bath with the help with Mr. Edward Aldred’s.

Solid state porphyrins@rGO complexes samples were used in TGA measurement which was then heated from room temperature up to 900°C at a rate of 2 °C per minute, with data points collected every 2 seconds under dynamic nitrogen flow (industrial grade, flow rate 100 ml min⁻¹). However, due to the small amount of porphyrins@rGO complexes measuring sample, which was round 0.1 mg - 0.2 mg, the measured results did not show very clear mass loss. Among all the measured results, only graphene oxide powder exhibited qualified measuring results. All TGA data were presented in Appendix A.
7.6 Standard protocol dye sensitised solar cells device build up.

The generation of a model dye sensitised solar cells device was carried out within Prof Lin Hong’s research group at Tsinghua University in Beijing, China. The standard fabrication process begins with a pre-process for fluorine doped tin oxide (FTO) glass substrate modification. A TiCl₄ solution (containing 22 ml TiCl₄ in 100 mL distilled water to make the stock solution, whereby the water needed to be replaced by same volume of ice due to the high reactivity of the TiCl₄) was prepared. The pre-prepared TiCl₄ solution was then diluted 50 times. The FTO was then merged in TiCl₄ solution and kept at 70 °C for 30 min.

The TiO₂ paste was generated by fully mixed TiO₂, ethyl cellulose and terpineol together. At least 1g TiO₂ (commercial product P25) should be used each generation branch. Since the density of P25 is relatively low, the P25 should be handled very carefully. The TiO₂ powder was then added into the ethanol solution, and a sonication bath was used in order to obtain a better dispersed solution.

![Terpineol](image)

The excess ethanol was removed under reduced pressure. The weight percentage of TiO₂, ethyl cellulose and terpineol is 18:9:73. The terpineol and ethyl cellulose were then removed following a heating progress. For the paste generation, a three-roll grinder was used to mix the three components together.

The TiO₂ paste was then coated onto a modified FTO substrate by a screen printing technique. The hole size of printed pattern was 0.4 cm × 0.4 cm. The thickness of coated layer can be adjusted depending on different dye molecules.
applied in the DSSCs system. During the printing progress, no glass was put under the plate in the first time, to make sure that all the screen holes can be filled with the paste. The modified FTO substrate was introduced afterwards and the printing progress were repeated 4 times with 6 min break after each operation.

A complex heating process was introduced to remove the organic solvents and stable the TiO$_2$ coating layer. The heating process included the following stages:

1. Increase the oven temperature from 30°C to 325°C within 30min and hold at 325 °C for 5min.
2. Increase the oven temperature from 325 °C to 375 °C within 5min and hold at 375 °C for 10min.
3. Increase the oven temperature from 375 °C to 450°C within 10 min and hold at 450 °C at 15min.
4. Increase the oven temperature from 450 °C to 500 °C with 5 min and hold at 500 °C at 15min.
5. Repeat the pro-process FTO modified progress and adjust the processing time to 20 min.
6. Increase the oven temperature from 30 °C to 500 °C within 50 min and hold at 500 °C for 15min.

The standard, commercial dye molecule N719 was applied as a 5 mM ethanol solution, which was generated with the aid of a sonication bath. The TiO$_2$ coated FTO substrates were then immersed in the dye molecule solution for 2 hours under 50 °C. The immersed time and the temperature can be adjusted according to different dye molecule. After the immerse process, the FTO was dried in air.
The electrolyte was made up by 0.5M TBP \(((\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_3\text{PO})\), 0.025M \(\text{I}_2\), 0.1M LiI and 0.6M 1-Propyl-3-methylimidazolium iodide (PMII) \((\text{C}_7\text{H}_{13}\text{N}_2\text{I})\) acetonitrile solution. Then, the cell was built up by assembling each layer together. Digital images of the generation process are provided in appendix C. Current experiments are being conducted in the laboratory of Prof Lin Hong using compounds 10 and compound 11, prepared hereby, as DSSC components using the protocol described hereby.

**7.7 Electrochemistry measurement**

The electrochemistry cyclic voltammetry measurements of non-covalently linked compound 11@SWNTs complex and covalently linked de-protected compound 11@SWNTs complex were carried out to detect their faradaic processes signals. The complexes samples were mechanical immobilised on the graphite electrode by grinding.

The measurements were carried out in 0.1M tert-butyl perchlorate in acetonitrile. Working electrode: 4.9 mm diameter basal-plane pyrolytic graphite
electrode, counter electrode: platinum wire, reference electrode: platinum wire with a \( \text{Cp}_2\text{Fe/Cp}_2\text{Fe}^+ \) solution.

Another measurement was carried out in 0.1 M \( \text{NaClO}_4 \) aqueous solution. Working electrode: 4.9 mm diameter basal-plane pyrolytic graphite electrode, counter electrode: platinum wire, reference electrode: Calomel electrode. All electrochemistry cyclic voltammetry data are presented in appendix E.

### 7.8 References to Chapter 7:

Appendix A: TGA data

**Figure A. 1** TGA curve obtained at the analysis of the graphene oxides (GO) synthesised. The graph is showing a loss of around 70 % weight, which may be associated with the evaporation of water absorbed onto the hydrothermally reduced GO surface. The weight loss began when the temperature arrived around 150 °C.

**Figure A. 2** TGA curve obtained at the analysis of the hydrothermally reduced graphene oxide (rGO) synthesised. The graph is showing a loss of 64 % weight, which may be associated with the evaporation of water absorbed onto the hydrothermally reduced GO surface. The weight loss began when the temperature arrived around 520 °C.
Figure A. 3 TGA curve obtained at the analysis of the hydrothermally synthesised compound 13@rGO complex. The graph is showing a loss of 75 % weight, which may be associated with the evaporation of water absorbed onto the GO surface and the compound 13 attached onto the hydrothermally reduced GO. The weight loss began when the temperature arrived around 550 °C.

Figure A. 4 TGA curve obtained at the analysis of the hydrothermally synthesised compound 14@rGO complex. The graph is showing a loss of 75 % weight, which may be associated with the evaporation of water absorbed onto the GO surface and the compound 14 attached onto the hydrothermally reduced GO. The weight loss began when the temperature arrived around 450 °C.
Figure A. 5 TGA curve obtained at the analysis of the hydrothermally synthesised compound 10@rGO complex. The graph is showing a continuously loss of weight, which may be associated with the evaporation of water absorbed onto the GO surface and the compound 10 attached onto the hydrothermally reduced GO. However, may due to the small scale sample used in the experiment, the result did not point out a precise temperature which indicates an obvious weight loss.

Note. Figures A. 1-5 exhibit the TGA measurement of free as-synthesised GO, the hydrothermally reduce rGO, compound 13@rGO complex, compound 14@rGO complex and compound 10@rGO complex. The TGA curve of graphene oxide presents a significant weight loss at 180 °C (the weight loss was more than 70 % wt.). After the GO was treated with porphyrins and hydrothermally reduced, both the rGO and porphyrins@rGO complexes presented weights loss at a higher temperature (around 550 °C). The increased temperature suggests that some of the oxygen containing groups and the surface defects originally present in the starting GO materials were removed. The TGA curve of compound 10@rGO did not show an obvious weight loss. This may due to the fact that only a small amount of sample was used in the measurement or the thermal resistance of the resulted nano-complex material was enhanced. The TGA measurement did provide evidence to the reduced reaction, but, due to the low resolution, it cannot offer conclusive information to the precise degree of the reduction and the weight percentage of porphyrin in the composite materials.
Appendix B: Microscopy images

Figure B.1 Additional TEM images of non-covalently linked compound 11@SWNTs (See Chapter 4, 4.2.1.1)
Figure B.2 Additional TEM images of covalently linked de-protected compound 11@SWNTs (See Chapter 4, 4.2.2.1)
Figure B.3 Additional HRTEM images (a)-(f) of as-synthesised graphene oxide by the JEM-2100 LaB6 TEM at Research Complex at Harwell. (See Chapter 2, 2.2.5.1)
Figure B.4 Additional HRTEM (a)-(e) images of thermally reduced graphene oxide (rGO) by the JEM-2100 LaB6 TEM at Research Complex at Harwell. (See Chapter 2, 2.2.6.2)
Figure B.5 Additional HRTEM (a)-(e) images of chemically and microwave-based reduced graphene oxide (rGO) by the JEM-2100 LaB6 TEM at Research Complex. (See Chapter 2, 2.2.7.2)
Figure B.6 Additional TEM (a) and (b) images of as-synthesised graphene oxide, the scale bar is 500 nm (left) and 50 nm (right). (See Chapter 2, 2.2.5.1)

Figure B.7 Additional TEM (a)-(b) images of thermally reduced graphene oxide (annealing at 1050 °C under hydrogen), both of the scale bars are 200 nm. (See Chapter 2, 2.2.6.2)
Figure B.8 Additional TEM (a)-(b) images of chemically and microwave-based reduced graphene oxide (rGO), both of the scale bars are 200 nm. (See Chapter 2, 2.2.7.2)

Figure B.9 Additional TEM (a)-(b) images of de-protected compound 11@GO complex, the scale bar is 50 nm (left) and 200 nm (right). (See Chapter 5, 5.2.1.1)
Appendix C. Standard protocol dye-sensitised solar cells (DSSCs) device build-up used during the training with Prof Lin Hong at Tsinghua University.

Figure C DSSCs device build-up process (a) FTO pro-process; (b) production of paste; (c) screen print TiO$_2$; (d) production of dye molecule solution; (e) immerse FTO in dye molecule solution; (f) Coated Pt on FTO, the details of this process were described in Chapter 7, 7.6.
### Appendix D. X-ray crystallography data

<table>
<thead>
<tr>
<th>Table D.1 Crystal data and structure refinement for the compound 10 discussed in Chapter 3. Data was collected and structure solved and refined by Dr. Sofia Pascu.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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| **Unit cell dimensions** | a = 13.4975(4) Å, α = 73.016(2)°  
                          b = 14.9537(5) Å, β = 81.9591(17)°  
                          c = 15.7807(5) Å, γ = 73.9566(13)° |
| **Volume** | 2921.51(16) Å³ |
| **Z** | 2 |
| **Density (calculated)** | 1.173 Mg/m³ |
| **Absorption coefficient** | 0.138 mm⁻¹ |
| **F(000)** | 1116 |
| **Crystal size** | 0.50 x 0.10 x 0.05 mm³ |
| **Theta range for data collection** | 2.139 to 25.058° |
| **Index ranges** | -16<=h<=15, -17<=k<=14, -18<=l<=15 |
| **Reflections collected** | 25186 |
| **Independent reflections** | 10191 [R(int) = 0.065] |
| **Completeness to theta = 25.058°** | 98.5 % |
| **Absorption correction** | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.99 and 0.99 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 4500 / 0 / 658 |
| **Goodness-of-fit on F²** | 1.1023 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0780, wR2 = 0.0817 |
| **R indices (all data)** | R1 = 0.1737, wR2 = 0.1140 |
| **Largest diff. peak and hole** | 0.88 and -0.36 e.Å⁻³ |
Table D.2 Crystal data and structure refinement for de-protected compound 11
disulphide-bridge dimer obtained as a side product. Data was collected and structure solved
and refined by Dr. Sofia Pascu.

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<th>Property</th>
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<td></td>
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<td>Density (calculated)</td>
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<td>Largest diff. peak and hole</td>
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Figure D.1 Molecular structure determination: a side product isolated after the prolonged air exposure of the de-protected compound 11 in aqueous DMSO emerges as a disulphide-bridge dimer (crystal structure was obtained by Dr Sofia Pascu).

Figure D.2 Molecular structure determinations: cell packing diagram, of the compound 11 disulphide-bridge dimer, view over axis a. Hydrogen atoms were removed for clarity. Note: The compound 11 molecules are oriented face-on and show two heptane chain groups placed anti with respect to the aromatic core. Thus, the disulphide-bridge compound 11 supramolecular structure shows weakly linked tubular arrangements of the dimeric molecules in the solid state.
Appendix E. Electrochemistry measurements

**Figure E.1** Cyclic voltammetry (scan rate 50 mVs\(^{-1}\)) of non-covalently linked compound 11@SWNTs complex (blue line) and covalently linked de-protected compound 11@SWNTs complex (red line) in 0.1M NaClO\(_4\) aqueous solution, working electrode: 4.9 mm diameter basal-plane pyrolytic graphite electrode, counter electrode: platinum wire, reference electrode: Calomel electrode.

**Figure E.2** Cyclic voltammetry (scan rate 100 mVs\(^{-1}\)) of blank environment (blue line), SWNTs complex (red line) and non-covalently linked compound 11@SWNTs complex (green line) in 0.1M NaClO\(_4\) aqueous solution, working electrode: 4.9 mm diameter basal-plane pyrolytic graphite electrode, counter electrode: platinum wire, reference electrode: Calomel electrode.
Figure E.3 Cyclic voltammetry (scan rate 10 mV s$^{-1}$) of blank environment (blue line) and non-covalently linked compound 11@SWNTs complex (green line) in 0.1M tert-butyle perchlorate in acetonitrile, working electrode: 4.9 mm diameter basal-plane pyrolytic graphite electrode, counter electrode: platinum wire, reference electrode: platinum wire with ferrocene/ferrocene + solution

From the recorded data shown in figure E.1 and E.2, relevant to an experiment carried out on samples of non-covalently linked compound 11@SWNTs complex and covalent linking de-protected compound 11@SWNTs complex in the dispersed phase using 0.1M NaClO$_4$ aqueous solution, it appears that the blank graphite electrode and the dispersed carbon nanotubes taken on their own did not show observable faradaic processes. This seems to suggest that under these conditions, no oxidized or reduced behaviour has been recorded, and all the represented processes observable by the measurement refers to capacitance of these nano-complex materials. This might due to the fact that compound 11 was not present in high enough concentrations for a observed a oxidation/reduction current to occur. These processes are diffusion-controlled so it is also likely that the access of the dispersed materials to the electrode was hampered by the low dispensability in the electrolyte used.

From the recorded data in figure E.3, relevant to the experiment which was carried
out using 0.1 M tert-butyle perchlorate in acetonitrile as the electrolyte, the extra peaks were probably from solvent contamination given that the 98-99% pure acetonitrile was used. The reference system is based on the Ferrocene/Ferrocene⁺ system which should only give a single reduction peak and an oxidation peak. By comparing the scans carried out with and without compound 11@SWNTs complex, there is no significant difference. As above, this might also due to the fact that compound 11 was not present in high enough concentrations for a observed a oxidation/reduction current to occur.
Appendix F. Raman spectroscopy measurements

Figure F.1: UV-vis spectra of non-covalently linked Compound 11@SWNTs complex (dispersed in 1:1 ethanol and chloroform solution, 1mg/mL), recorded from 225 nm to 670 nm. The broad peak emerge at around 275 nm was due to the well dispersed functionalised SWNTs in the solution.

Figure F.2: UV-vis spectra of covalently linked Compound 11@SWNTs complex (dispersed in 1:1 ethanol and chloroform solution, 1mg/mL), recorded from 300 nm to 670 nm. The broad peak emerge at around 315 nm was due to the well dispersed functionalised SWNTs in the solution.
Appendix G. Mass spectroscopy of metalloporphyrin

Figure G.1: The Mass spectroscopy (MALDI) of In(III)-porphyrin (Compound 11a).

Figure G.2: The Mass spectroscopy (MALDI) of Ga(III)-porphyrin. (Compound 11b)
Appendix H. UV-visible spectroscopy

Figure H.1: UV-visible absorbance titration of coronene and Zn(II)-porphyrin (compound 11), spectra from 520 nm-620 nm, see Chapter 4, 4.2.1.6.

Figure H.2: UV-visible absorbance titration of GO and Zn(II)-porphyrin (compound 11), spectra from 510 nm – 660 nm, see Chapter 5, 5.2.1.5.
Appendix I. synthesis of In(III) and Ga(III) porphyrin

In comparison with Zinc(II) salt precursor used, InCl$_3$ and GaCl$_3$ salt are both more air sensitive, requiring a sealed oxygen free atmosphere. The atom size of Indium and Gallium are also bigger than that of Zinc, which leads to the space in tetradeutate ligand being hard to trap the metal centre. If the ionic radius of the metal ions is too large, (e.g. for Indium, (over ca. 80-90 pm)) this makes it more difficult to fit into the centre of the macrocycle, and they are located outside of the ligand plane. This causes a higher reactivity of the complex. The symmetry of those porphyrins is lower (generally $C_4v-C_1$) than that of both the free base porphyrin ($D_{2h}$) and the Zn(II)-porphyrin ($D_{4h}$), in which the metal centre fits into the ligand cavity. All above reasons made the Indium and Gallium metalation of free base porphyrin to become more challenging, especially when the general method introduced for Zinc metalation of free base porphyrin was adapted.

![Diagram](image.png)

**Figure I.1:** Schematic diagram of metalloporphyrins generation, In(III)-porphyrin (compound **11a**) and Ga(III)-porphyrin (compound **11b**).

In order to find out a unique the method which can be applied to different metal
centres as well as the free base porphyrin, a microwave reaction was introduced, whilst using dry DMF as the alternative solvent. In this project, Indium(III) chloride and Gallium(III) trichloride were used as metal salts and handled in a glove box under Argon. The reactions were carried out at 150 °C for 10 minutes in the microwave. After purification, the resulting materials were analysed by $^1$H NMR and Mass spectrometry, and their UV-Vis spectroscopy recorded and compared to that of the free base porphyrin 10 and Zn(II)-porphyrin 11 (all in 1 μM solvents in ethanol).

**Ultraviolet-visible spectroscopy of metallised porphyrins**

The Ultraviolet-visible (UV-vis) spectroscopy measurement was carried out to investigate the different light absorption behaviour of the four different porphyrins. The absorption spectroscopies of the free base porphyrin, Zn(II)-, In(III)- and Ga(III)-porphyrin were recorded. It can be found from the measured results that the Soret band of Ga (III)-porphyrin, Zn(II)-porphyrin and In(III)-porphyrin was observed at 414 nm, 417 nm and 418 nm respectively, which were, in all cases due to an electron dipole movement allowing $\pi-\pi^*$ transition. Compared to the case of free base porphyrin 10, all those three metallised porphyrins presented red shift in the Soret absorption band. The secondary absorption bands of Ga (III)-porphyrin, Zn(II)-porphyrin and In(III)-porphyrin were also presenting differences comparing with free base porphyrin: for metallised porphyrins, the three secondary absorption bands observed in free base porphyrin were substituted to one main absorption peaks. The different light absorption behaviour recorded at secondary absorption bands, were due to the interaction between the centre metal atoms interacts with the porphyrin conjugate electrons.
Figure I.2: (a) Ultraviolet-visible spectroscopy of free base porphyrin (10), Zn(II)-porphyrin (11), In(III)-porphyrin and Ga(III)-porphyrin (in 1 μM solvents in ETOH); (b) Enlarged area of conditions UV-vis spectra of Figure (a).

The comparison of the three metallised porphyrin, the measured results established that Ga (III)-porphyrin, In(III)-porphyrin and Zn(II)-porphyrin all exhibited a competitive light absorption behaviours in visible light region, which means the molecule can potentially convert absorbed light into qualified energy to excite electrons from low energy level jumping to high energy level. Zn(II)-porphyrin was chosen to carry out further
experiments due to the less air sensitive during the synthetic procedure.

To study the light absorption behaviours of metallised porphyrins, UV-vis spectroscopy was an appropriate powerful characterised method. Firstly, the UV-vis measurement can tell the differences among light absorption behaviour of metallised porphyrins; secondly, it can provide a direct view of the large range of visible light absorption property regarding metallised porphyrins as light harvesting molecule; thirdly, after further interacted with carbon nanomaterials, the prospective blue or red shifted of Soret band together with an emerging peak appears in Soret band or secondary absorption peak region can present a straight evidence of the formation of new nanohybrids system or complexes material.

**Spectroscopic characterisation by FTIR**

The FTIR spectroscopy was carried out to identify the abundance of different type chemical bonds appeared in the four types of metalloporphyrins. Figure I.3 is the recorded results. From Zn(II)-porphyrin (compound 11), the axil was set as transmittance, a peak emerges at 1264 cm\(^{-1}\), which corresponds to C-N stretching band of the amide group. The peaks at 1456 cm\(^{-1}\), 1495 cm\(^{-1}\) and 1630 cm\(^{-1}\) are representative of carboxylate groups. The peak appearing at 1711 cm\(^{-1}\) is the C=O stretching vibration. Similar measured results can be observed in Ga(III)-porphyrin. However, compared In(III)-porphyrin with compound 10, the peaks didn’t show a big change. The FTIR measuring data was partly demonstrate the formation and molecule structure of Zn(II)-porphyrin.
To further investigate whether the microwave method is efficient for the synthesis of metalloporphyrins, HPLC characterisations of the resulting materials were carried out. The measurement results are shown in Figure I.4. The peak appeared in between 2-2.5 min were due to the injection of samples in DMSO, but the peaks at 2.5-3.5 min are arguable into the ligand for M(OH)$_n$ species ($n$=2,3, M=Zn(II), Ga(III), Ga(III)). Free base porphyrin did not show the peak in the 2.5-3.5 min, and presented a main peak at 14.697 min, which means the free base porphyrin was majorly pure. For Zn(II)-porphyrin, similar measured result can be observed: there was a main absorption peak at 14.707 min. For Ga-porphyrin, the main absorption peak was at 14.733 min but the intensity was much lower compared with other metalloporphyrins investigated. It may due to the hydrolysis of the Ga(III)-porphyrin species with the HPLC conditions, and Cl/CF$_3$COO/OH in solution. For In-porphyrin, the HPLC measurement exhibited two absorption peaks at 14.587 min and 15.437 min, it indicated that in In-porphyrin sample, the final product is not pure and contained two
different containing materials. This could mean that the 5th-coordination site at In(III)-porphyrin may have been exchanged from Cl to CF$_3$COO$^-$ or OH counter-ion on the measurement of HPLC alone this cannot be certain.

![HPLC Chromatograms](image)

**Figure I.4**: HPLC of free base porphyrin, Zn(II)-porphyrin, Ga(III)-porphyrin and In(III)-porphyrin. ($\lambda_{\text{abs}}$=400 nm).
Appendix G. Graphenisation of electrospun poly-acrylonitrile nanofiber

This side project of graphenisation of electrospun poly-acrylonitrile nanofiber was carried out due to a collaboration with Prof Frank Marken. Electrospun poly-acrylonitrile nanofiber has recently employed to generate “bucky paper” nanocarbon membranes, which exhibited limited stability towards swelling and degradation during electrochemical processes. To enhance the electrochemical reactivity and conductivity of poly-acrylonitrile nanofiber membrane, graphene oxide synthesised as described in this project (Chapter 2 and Chapter 7) was applied as a precursor of a graphitic film.

Figure G.1: Schematic drawing of (a) ITO coating process addresses a graphitic coating (GO-C), a carbonised nanofiber coating (ES-C), and a combined carbonised nanofiber – graphitic coating (ES-GO-C); (b) Coating of borosilicate glass capillary tubes with a combined carbonised nanofiber – graphitic coating (ES-GO-C). (This data was published during the thesis preparation. See reference 30 for more details)

Carbon nanofibres are conveniently prepared by electrospinning and deposited onto Indium Tin Oxide (ITO) coated glass surface (Figure G.1). Carbonisation was then carried out at a relatively mild temperature (500 °C). Electrochemical reactivity was investigated
with and without the addition of the graphene oxide which coated the surface of ITO prior to carbonisation. Graphene oxide was coated onto the fibre membrane by a dip coating method which was chosen due to its simplicity, efficiency, and economy, and then the sample was carbonised.

Figure G.2: SEM images for (a) and (b) electrospun PAN nanofibres after carbonisation, the scale bar = 1μm and 100 nm respectively; (d) and (c) electrospun PAN nanofibres dip coated in GO, and then carbonised, the scale bar = 1μm and 100 nm respectively. (This data was published during the thesis preparation. See reference 30 for more details)

Figure G.2 presented the SEM images of carbon nanofiber coating with and without graphene oxide. From the recorded images, graphene oxide was deposited onto the carbon nanofiber network and forms a sheet like membrane on the surface of the nanofiber network. Following cyclic voltammetry measurement confirmed that graphene oxide can enhance the electrochemical reactivity and conductivity of the nanofiber. This data is of
relevance to the construction of more homogenous materials for future photovoltaic applications.